Physics

SCIENCE OF LIGHT

VOLUME 4 NUMBER 1

August

1955

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SCIENCE OF LIGHT

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Printed by
Kokusai Bunken Insatsusha
Chiyoda-ku, Tokyo.

A New Method on Infrared Photography

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(Received Feb. 1, 1955)

As the ordinary method of taking infrared photographs becomes useless to wave-lengths greater than 1.4 μ, Czerny invented in 1929 an interesting method applicable to radiation of any wave-length. The authors found another method which is based on a principle different from Czerny's. A thin membrane is blackened on one side with metal black, and the space on the other side is filled with aerosol. Parts of the membrane where the radiation impinges are warmed up, so that the particles of the aerosol cannot approach there. Thus the image of a body to be photographed is formed on the membrane. This image can be made clearer by a devised developing process. By this method absorption spectra of some organic liquids were obtained. The sensitivity is practically the same as that of ordinary thermopiles. The definition of the image is at present inferior to that by Czerny's method.

1. Introduction

As is well known, ordinary photographic plates are not sensitive to infrared rays. Although there are many attempts to increase the sensitivity of the plates in infrared region, it is at present impossible to render emulsions sensitive to wave-length beyond 1.4 μ[1]. Czerny showed from theoretical considerations that this might be the limiting boundary of sensitisation[2]. Indeed one can extend this limitation by using the so-called phosphoro-photography, but this also fails beyond 2 μ. In 1929, suggested by the Hershel's experiments[3], Czerny invented an ingenious method of taking infrared photographs called "evaporography"[4]. He used a very thin membrane which was blackened on one side with metal black, and coated on the other side with materials such as paraffin oil having a high vapour pressure. The radiation that impinges upon the black

1) O. Masaki and T. Morita, Journ. Hiroshima Univ. **7**, (1937), 305.
T. Suga, M. Kamiyama and T. Sugiura, Sci. Pap. I.P.C.R. **34**, (1937), 32.
2) M. Czerny, ZS. f. Phys. **53**, (1929), 1.
3) J. F. W. Herscel, Phil. Trans. **131**, (1840), 52.
4) See reference (2)
H. Willenberg, ZS. f. Phys. **74**, (1932), 663.
G. Moench und H. Willenberg, Ibid, **77**, (1932), 170.
M. Czerny und P. Mollet, Ibid, **108**, (1937), 85.
J. Lecomte, J. Phys. Radium, **10**, (1949), 27.

side of the membrane, is absorbed by it and raises its temperature. Therefore the volatile substance on the other side evaporates away from the warmer parts of the membrane and deposits on the cooler places. Thus the parts of the coating on which the radiation impinges become thinner, and the image of the object to be photographed is obtained. This method in its improved form is very sensitive, capable of integrating the effect of radiation and applicable to radiation of any wave-length, but it has not come into common use because the technics required are rather difficult.

While studying Czerny's method the authors found another simpler method applicable to the infrared beyond a few microns.

2. Principle of the Method

A very thin membrane is blackened on one side with metal black and put into an enclosure with a window. The space on the other side is filled with aerosol of NH_4Cl or cigarette smoke (Fig. 1.) Infrared rays which fall upon the blackened surface of the membrane are absorbed by it and raise its temperature. The particles of aerosol gradually settle on the membrane excepting the parts where the temperature is higher.

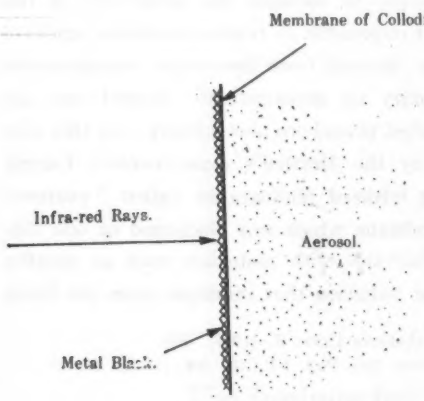

Fig. 1.

Thus the parts on which the radiation impinges become clear, forming the image of the object. This image can be made more distinct by a developing process which consists essentially in evaporating zinc on the membrane at a pressure between 10^{-2} and 10^{-3} mm Hg. The evaporated metal does not condense on the parts of the surface where the particles of aerosol have settled, while on the parts, where the particles are absent, it forms a thin film and shows metallic reflection, thus making the image appear distinctly. The cause of this may be that, at least in the case of cigarette smoke, some organic matters contained in the smoke containate the surface of the membrane preventing the condensation.

In the present experiment, mist of NH_4Cl and cigarette smoke were adopted

as the aerosol. The former gives superior image but is inferior in sensitivity to the latter.

The temperature during exposure is one of the important factors that affects the results. When the ambient temperature exceeds about 25°C, no image is formed on the membrane, necessitating cooling of the apparatus. On the other hand, when the temperature is too low, no good image seemed to be obtained either.

The reason why the aerosol particles cannot approach the warmer parts of the membrane is as follows. An aerosol particle in a gas of non-uniform temperature is subjected to a thermal force which causes the migration of the particle down the temperature gradient. Thus a "dark space" is observed around a hot body placed in an illuminated chamber of dust-filled air. There are many investigations concerning this remarkable phenomenon, and according to Epstein[5] the thermal force F_t acting on a spherical aerosol particle is

$$F_t = -9\pi(D_p/2)(\mu^2/\rho T)[k_a/(2k_a+k_t)]G(\text{dyne})$$

where the following notations are employed.

D_p=particle diameter, cm.

μ=air viscosity, g mass/cm-sec.

ρ=air d nsity, g mass/cm^3.

T=absolute temperature, deg K.

k_a=thermal conductivity of the gas, cal/sec-cm-deg K.

k_t=thermal conductivity of the sphere, cal/sec-cm-deg K.

G=temperature gradient prevailing in the gas, deg C/cm.

Recently, Saxton and Ranz[6] made a thorough investigation of this thermal force, and found that their experimental results were in good agreement with Epstein's formula.

In the present experiment a temperature gradient is built up near the membrane on which radiation is impinging, and the aerosol particles are repelled off by the thermal force stated above.

3. Apparatus

The apparatus used in the experiment is shown in Fig. 2. The chamber is water-jacketed to prevent thermal disturbances and to maintain it at a suitable constant temperature.

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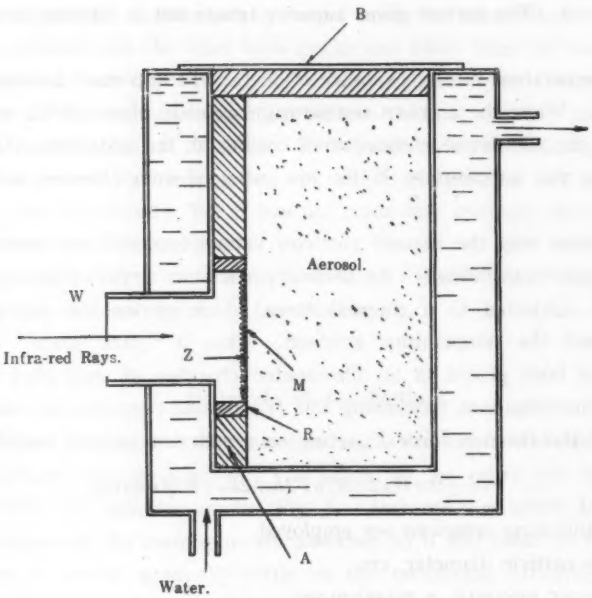
5) P. Epstein, ZS. f. Phys. **54**, (1929), 537.

6) R. L. Saxton and W. E. Ranz, J. Appl. Phys. **23**, (1952), 917



M: Membrane of Collodion
Z: Metal black
W: Window
R: Brass ring
B: Lid
A: Frame supporting the brass ring

Fig. 2.

The membrane of collodion is stuck on the brass ring R, and blackened on one side with bismuth black. After this ring is fixed into the frame A, the chamber is carefully filled with aerosol, and then covered with the lid B. Another collodion film is stuck on the window in order that the stream of the external air may not disturb the temperature distribution of the membrane while being irradiated through the window.

The membrane of collodion can be obtained according to Czerny's method[7], by dropping a solution of collodion in amyl-acetate onto the surface of a bowl of dust-free water, and by picking up with a metal frame as soon as the solvent has evaporated. Such a film is extremely thin, and is suitable for the purpose.

To blacken the membrane, bismuth was evaporated in a low vacuum after the method of Pfund[8]. Czerny also adopted this method in his experiment. In

7) See reference (4)
8) A. H. Pfund, R. S. I. **1**, (1930), 379.
J. O. S. A. **23**, (1933), 375.

this case a block of metal of a large heat capacity must be placed colse to the opposite side of the membrane. (about 0.1 mm apart) Without this block the temperature of the membrane becomes so high during evaporation that no bismuth black is formed on its surface.

4. Results Obtained

Fig. 3 shows the image of the filament of a 250-watt projector lamp obtained by this method. The distance between the lamp and the camera was about 80 cm.

Fig. 3.

The six short lines in the center represent the filament, and the long streaks running upwards are the loci of the ascending air current that was produced from overheating of the film by the intense incident light. In this experiment mist of NH_4Cl was used as aerosol.

Fig. 4 shows the absorption spectra of some organic liquids. The radiation source was a 200-watt projector lamp. The spectrometer used was a Wadsworth type equipped with a quartz prism. The diameter of the mirror was 4 cm, whose focal length was 40 cm. The slit width was about 0.1 mm. The time of exposure was between 30 and 60 minutes.

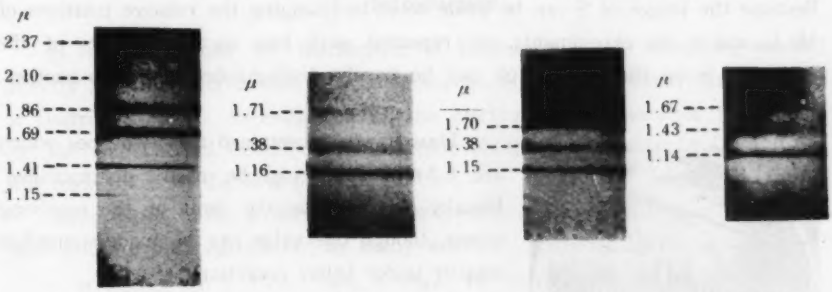


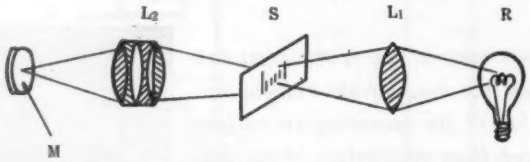
Fig. 4.

These spectra are all very similar and possess pronounced absorption bands at 1.2 μ, 1.4 μ, 1.7 μ which are interpreted as the overtones of C–H vibrations. These photographs are in good agreement with the results obtained by thermopile[9]. In this experiment cigarette smoke was employed as aerosol.

9) J. W. Ellis, Phys. Rev. **23**, (1924), 48.

5. Sensitivity and Definition of the Image

The sensitivity and the definition by this infrared photography depend considerably upon the manner of blackening the membrane and of evaporating zinc, that is, upon the developing process. Generally speaking, the sensitivity of this method is similar to that of the ordinary thermopiles. As this method can integrate the effects of radiation, it might be supposed more sensitive than with other infrared detectors. But unfortunately the expected results could not be obtained.



M: Membrane of Collodion
L_2: Camera Lens
S: Glass Scale
L_1: Condenser Lens
R: Light Source

Fig. 5.

To examine the definition of the image, the arrangement as shown in Fig. 5 was employed. The light from the source R is collected by the lens L_1, and illuminates the glass scale S. The sharp image of the source must not be formed on this scale. S is made by printing a scale on a photographic plate, and only the lines of the scale are transparent. The image of S is projected on the membrane M by the lens L_2. M is carefully protected from stray light. Because the image of S can be made small by changing the relative positions of M, L_2 and S, the experiments are repeated until two successive lines of the image of S on the photograph can be barely distinguished from one another. (Fig. 6)

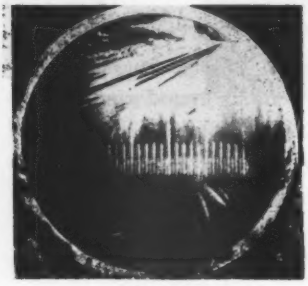


Fig. 6.

Thus it was ascertained that two lines which are 0.3 mm apart can be easily distinguished. Usually this may be the limit of the resolving power, though this value can be made somewhat smaller under better conditions.

6. Conclusion

In spite of its simplicity, the above-stated method on infrared photography gives fairly good results. Although it is not yet satisfactory in the present state, it will be possible to increase the sensitivity and definition of the image by selecting proper aerosol and by improving the method of development.

On the Luminescent Behaviors of ZnS Phosphors under the Influence of A.C. Electric Field

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(Received May 6, 1955)

The Gudden-Pohl effect of some electroluminescent phosphors ZnS:Cu and ZnS:Mn has been investigated. Several behaviors of the phosphors shown under the influence of A.C. electric field are reported and discussions on the results obtained are given. These phosphors had been kept in darkness at a room temperature for a definite time after the ceasing of the irradiation of continuous ultra-violet radiation ranging from 3300Å to 3900Å and then a 60 cps A.C. electric field was applied. The Gudden-Pohl luminescence thus obtained is observed mainly by means of a cathode-ray oscilloscope. Some qualitative features of their "Auslöschung" phenomena are ascertained. From close investigations of the oscillograms, the "Auslöschung" of ZnS:Cu at "field on" is observed as stimulation and quenching luminescence depending on the field intensity, and in ZnS:Mn the field dependency of the stimulation is also observed. It is also suggested that the light sum of the phosphor luminescence may be measurable.

The mechanism of the electroluminescence and that of electrophotoluminescence are considered probably different from each other in their excitation processes.

1. Introduction

In order to study the mechanism of luminescence of phosphors excited directly by A.C. electric field (this phenomenon is known as electroluminescence or Destriau's effect), investigation of the electrophotoluminescence phenomena (or the Gudden-Pohl effect) of zinc sulphide phosphors activated by Cu and Mn was undertaken in the first place.

With respect to the problem of electrophotoluminescence, various investigations have hitherto been carried out by many workers[1]. Among them, especially, F.

1) B. Gudden and R. Pohl: Zeits. f. Phys., **17** (1923), 334.
G. Destriau: J. Chim. Phys., **34** (1937), 327.
G. Destriau: Phil. Mag., **38** (1947), 880.
G. Destriau: J. Appl. Phys., **25** (1954), 67.
E. Matossi and S. Nudelman: Helv. Phys. Acta., **26** (1953), 573.
F. Matossi and S. Nudelman: Phys. Rev., **89** (1953), 660.
K. W. Olson: Phys. Rev., **92** (1953), 1323.
W. Low, J. T. Steinberger and E. A. Braum: J. Opt. Soc. Am., **44** (1954), 504.

Matossi[2] explained the phenomenon quantitatively by some mathematical analyses. It will be worthy of note that most of phosphors used in these experiments were ZnS, CdS and SrS families, all of which showed the infra-red responsive behavior.

The above investigators used U.V. radiation or X-rays as the irradiation source and high D.C. or A.C. electric field was applied during the irradiation or immediately after it has been removed.

2. Materials and Experimental Procedures

The samples used in the present experiments are ZnS phosphors activated by Cu (8×10^{-5} weight %) or Mn (1×10^{-3} weight %). The former shows a comparatively long duration of after-glow (about several ten minutes), while the latter short persistence (only about ten seconds). The temperature and duration for the crystallization of the samples are given in Table 1. Their phosphorescence spectra taken with a constant deviation prism spectrograph are shown in Fig. 1. As seen in Fig. 1, α band (5260Å) is predominated in ZnS:Cu, while δ band (5900Å) in ZnS:Mn.

Table 1. Crystallization Temperature and Duration, and Luminescence Thresholds of the Sample Phosphors.

Phosphor	Temerature of Crystallization	Duration of Crystallization	Threshold Strength of Eelctrophoto-luminescence	Threshold Strength of Electrolumi-nescence
ZnS:Cu	1250°C	60 min	2.3×10^{3} V/cm	6.2×10^{4} V/cm
ZnS:Mn	950°C	30 min	2.1×10^{3} V/cm	5.1×10^{4} V/cm

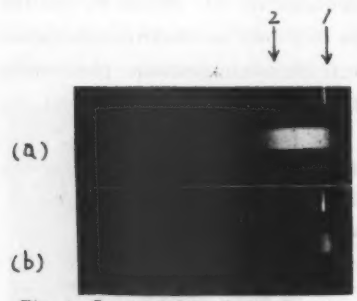


Fig. 1 Spectral Distribution of the Sample Phosphors.
(a) ZnS:Cu, (b) ZnS:Mn. The arrow 1 is Na D-line (5890Å), and 2 is Cd (4811Å).

It is supposed that both phosphors show the infra-red responsive behavior[3].

An electroluminescent cell was prepared in the following manner. The phosphor, after pulverized in an agate mortar, is mixed into semi-polymerized polymethylmetacrylate. The upper portion, composed of the finest powders left by sedimentation, is poured onto a thin mica plate of about 0.05 mm in thickness, and dried and polymerized in an Acme electric oven at 60°C for half a day, the final thickness becoming

2) F. Matossi: Phys. Rev., **94** (1954), 1151.
3) G. R. Fonda: J. Opt. Soc. Am., **36** (1946), 382.

about 0.05 mm. The sheet thus obtained is sandwiched between two BK7 glass plates. As electrodes, the whole inner side of one of the plates and only the borders of the other are coated with double layer of Cu and Ag by vacuum evaporation. The clear part of the latter is wetted with a mixture of NaCl solution and glycerine to render it conductive yet transparent to view the luminescent radiance and to transmit U.V. light.

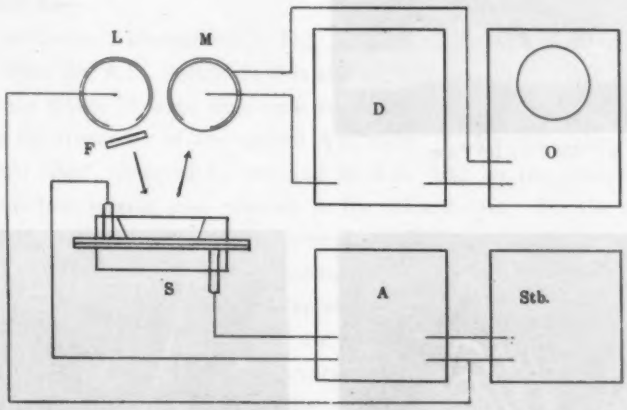


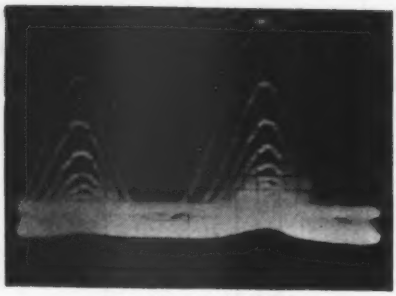
Fig. 2 Schematic Diagram Illustrating the Experimental Arrangement.
L: Incandescent Lamp, 100 V, 100 W. F: Matsuda's UVD-2 Filter.
M: RCA Multiplier Phototube. D: D.C. Supply.
A: A.C. Supply. O: Cathode-Ray Oscilloscope.
Stb: A.C. Voltage Stabilizer.

To take the oscillograms of the Gudden-Pohl effect of the phosphors, an arrangement shown schematically in Fig. 2 was employed. An U.V. source of radiance was obtained by filtering the temperature emission from an incandescent lamp (fed by 100 V A.C. 100 W, whose voltage was well stabilized within ±0.5 volts) by a Matsuda's UVD-2 filter. Accordingly, the exciting light thus obtained was continuous in spectrum from about 3300Å to 3900Å. After 1 min. irradiation of the U.V. light, the phosphor was kept in darkness for a certain time t. With the application of an A.C. electric field of 60 cps, $2\times10^3\sim 2\times10^6$ V/cm, the phosphor then showed a momentary illumination or quenching.

The Gudden-Pohl luminescence was received by a RCA multiplier phototube 1P28. D.C. high voltage, which was applied on the tube, was obtained with a circuit of L. U. Hibbard and D. E. Caro[4], constancy of the voltage being whithin ±1 volt per 1000V. The out-put of the photomultiplier was fed to the vertical

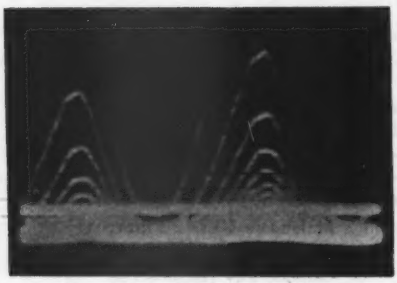
4) L. U. Hibbard and D. E. Caro: J. Sci. Instr., **30** (1953), 378.

[A]

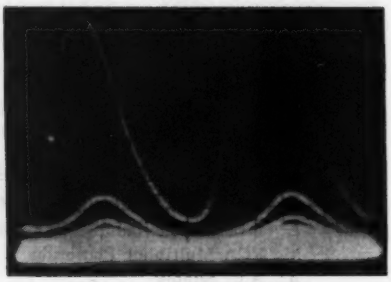


(a) $E=2.6\times10^4$ V/cm

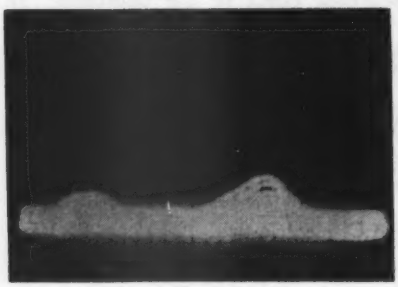
[B]



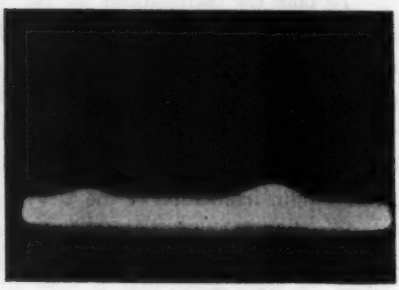
(b) $E=4.4\times10^4$



(b′) $E=2.9\times10^4$



(c) $E=4.4\times10^4$



(c′) $E=2.9\times10^4$

Figs. 3–A and 3–B.
(a), (b) and (b′) are the 1st stimulations for t=30 sec;
(c) and (c′) are the 2nd, 15 sec after the termination of the 1st.

plates of a cathode-ray oscilloscope, whose horizontal sweep being synchronized with the cycle of the A.C. field, i.e. one sixtyth of a second. The oscillograms thus obtained are shown in Figs. 3-A and 3-B.

3. Results and Discussions

(1) *Qualitative features of Gudden-Pohl luminescence*

(a) ZnS:Cu

The oscilloscopic photograms in Fig. 3-A are obtained for ZnS:Cu, t being 30 sec. When the A.C. electric field is applied, sharp quenching and remarkable luminescence waves of large amplitude are overlapped, the latter fluctuating in just twice the frequency of the applied A.C. field. F. Matossi's theory[2] on the Gudden-Pohl effect, observed by applying an A.C. field on the phosphor during U.V. irradiation, seems also relevant in the present case. But the phenomena seem to depend largely on the field intensity. With a weak field, quenching is predominant, and when the field intensity increases, the luminescence waves become so noticeable that the case appears as of stimulable one. Photograms taken with increasing field intensities are shown in Fig. 3-A. When the field is removed, the after-glow partly recovers. These features mentioned above are in accord with K.W. Olson's observation on ZnS/CdS:Cu except that, with the 2nd manipulation of the field, the stimulation and quenching were again observed in the present case but only quenching by Olson.

(b) ZnS:Mn

The photograms shown in Fig. 3-B were taken with ZnS:Mn, $t=30$ sec. In this case, owing to its short persistency, no quenching was noticed and the predominant stimulation luminescence was always there. Compared with the stimulation luminescence of ZnS:Cu, which continues up to several ten cycles, that of ZnS:Mn fades very rapidly surviving only a few cycles. In ZnS:Mn, the 2nd stimulation was also observed when the electric field was again applied. But when the initially applied field was sufficiently intense, no 2nd stimulation was observed.

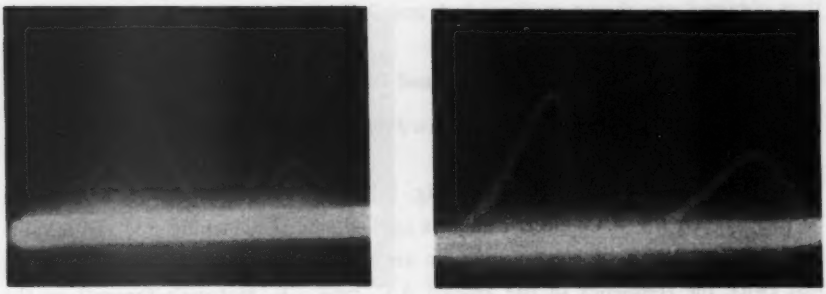
The minimum intensity of the A.C. field inside a phosphor sphere E necessary to stimulate the electrophotoluminescence (the Gudden-Pohl effect) is calculated by means of the formula given by S. Roberts[5]

$$E=E_m\cdot 3k_1/\{2k_1+k_2-V_2(k_2-k_1)\}$$

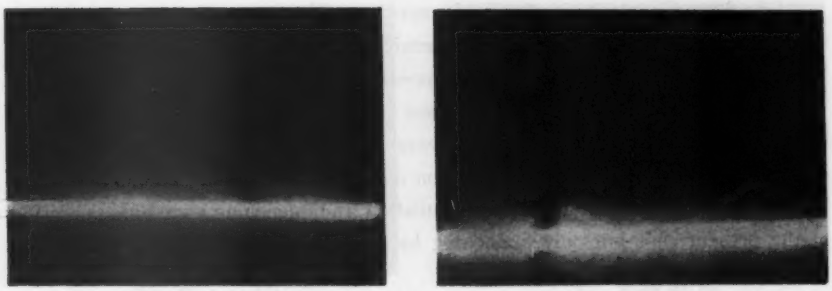
where E_m is the potential gradient applied to the phosphor-dielectric mixture, k_1 and k_2 dielectric constant of a matrix and of a single sphere of homogeneous

5) S. Roberts: J. Opt. Soc. Am., **42** (1952), 850.

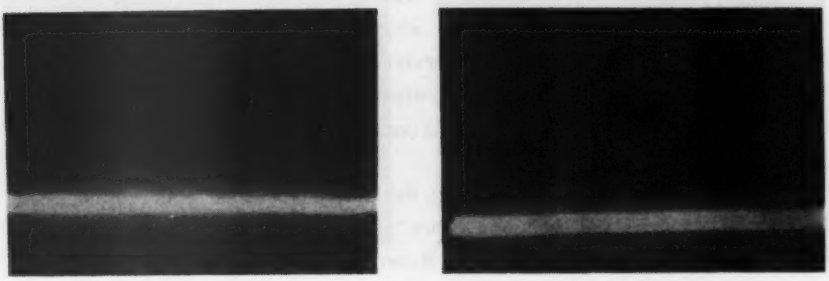
[A] [B]



(a) $t=1$ min. (a′) $t=1$ min.

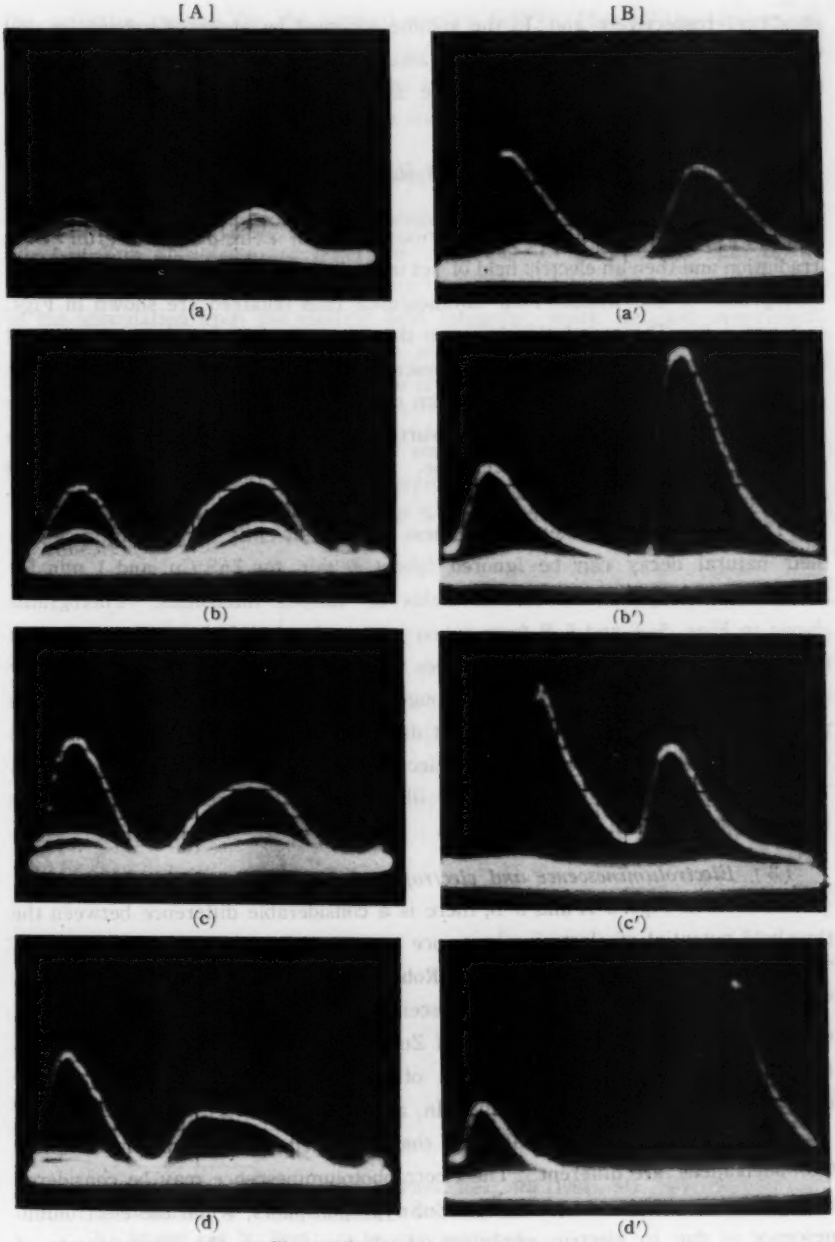


(b) $t=10$ min. (b′) $t=10$ min.



(c) $t=1$ hour. (c′) $t=30$ min.

Figs. 4–A and 4–B
Field intensity E is kept constant.



Figs. 5–A and 5–B. $t=5$ min.

(a) $E=1.7\times10^4$ V/cm, (a′) $E=1.5\times10^4$ V/cm,
(b) $E=4.4\times10^4$ V/cm, (b′) $E=3.6\times10^4$ V/cm,
(c) $E=6.1\times10^4$ V/cm, (c′) $E=5.1\times10^4$ V/cm,
(d) $E=8.8\times10^4$ V/cm, (d′) $E=7.3\times10^4$ V/cm.

phosphor, respectively and V_2 the volume occupied by phosphor spheres in unit volume of the mixture. V_2 may be assumed here as 1/2. The results thus obtained are shown in Table 1. The E values for ZnS:Cu and ZnS:Mn are nearly the same.

(2) *Possibility of measuring the light sum and electric field responsive behaviors*

The phosphors were kept for various duration t in darkness after U.V. irradiation and then an electric field of set intensity was applied. The oscilloscopic photograms of the Gudden-Pohl luminescence thus obtained are shown in Figs. 4-A and 4-B. The correlation between the duration of time t in darkness and the height of the stimulation luminescence of the phosphors may well be perceived in the figures. The light sum of the phosphor luminescence may be considered as proportional to the area surrounded by the curves of the stimulation luminescence waves and the sweep line. But to measure the area, well defined curves have to be obtained.

The phosphors were kept in darkness for a sufficiently long time in which their natural decay can be ignored (about 5 min for ZnS:Cu, and 1 min for ZnS:Mn), then placed in electric fields of various intensities. Photograms shown in Figs. 5-A and 5-B were taken with $t=5$ min. It is worth mentioning that the area of the luminescence waves is the largest at a certain field intensity and becomes smaller with both stronger and weaker intensities. This is probably attributed to the predominant draining effect[2] in strong field while, in weak field, only a limited number of electrons in the phosphor trap are excited. Thus the brightness of the momentary illumination is a function of the electric field intensity applied on the phosphor.

(3) *Electroluminescence and electrophotoluminescence*

As seen in Figs. 5-A and 5-β, there is a considerable difference between the threshold potential of electroluminescence and that of electrophotoluminescence. The threshold values calculated by S. Roberts' formula are given in Table 1. The threshold value of electroluminescence is 27 times larger than that of electrophotoluminescence in the case of ZnS:Cu, while 24 times in ZnS:Mn. On the other hand the threshold values of electrophotoluminescence are nearly the same for both ZnS:Cu, and ZnS:Mn, as mentioned in (1).

These facts may certainly indicate that the excitation mechanisms of these two phenomena are different. The electrophotoluminescence may be considered as due to electron traps peculier to ZnS-type phosphors, while the electroluminescence as due to electric excitation of electrons from the normal state of

the activator centres by the applied electric field[6]. Thus all the luminescent behaviors of ZnS phosphors excited by an A.C. electric field may well be interpreted. This consideration may be supported also by the observed spectral distribution of the electroluminescence and the radiant appearances[7].

4. Conclusion

Some features concerning the "Auslössung" phenomena in the Gudden-Pohl effect of ZnS phosphors are described. For measuring the light sum of the phosphor luminescence from stimulation curves and determining the dependency of the stimulation upon the electric field intensity, more detailed experiments and theoretical treatment are to be made. Excitation process of electrons contributing to the electroluminescence is not yet clear for which investigations are now in progress.

The authors wish to express their sincere thanks to Chigasaki Works of the Dai Nippon Toryo Co. for kindly supplying the phosphor samples. This experiment was financially supported by the Scientific Research Fund of the Ministry of Education.

6) J. F. Waymouth and F. Bitter: Phys. Rev., **95** (1954), 941.
7) G. Destriau: J. Phys. Radium., **15** (1954), 13.
K. Asagoe and N. Tani: to be soon published.

On the Infrared-Responsive Behaviors of (Zinc: Cadmium-Sulphide: Selenide)-Type Phosphor Families*

III. Zinc-Sulphide: Selenide Phosphors (2)

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(Received Feb. 21, 1955)

Some singly or doubly activated cubic or hexagonal zinc-sulphide: selenide phosphors have been prepared. Their spectral infrared-responsivity and spectral distribution of luminescence as well as their crystal structure are investigated. The obtained results are compared with those on other zinc-sulphide: selenide phosphors, which are reported in the previous paper. Further, they are explained qualitatively by a model, which contains two types of electron traps, namely traps associated with emission centers and isolated traps.

1. Introduction

The luminescence and the infra-red (abbreviated as ir) responsivity of some cubic zinc-sulphide: selenide (abbreviated as Zn(S:Se)**) phosphors have already been investigated[1]. In the present paper are reported the results of similar researches on some of the other Zn(S:Se) phosphors.

The pure ingredients, ZnS and ZnSe, were prepared by means of the chemical processes described in the previous papers[1][2]. ZnSe powder thus prepared was dissolved in conc. pure HNO_3 contained in a porcelain basin on a sand-bath. Then a slow evaporation was continued until deposited solids appeared sufficiently dried. They were dissolved again in distilled water and the quantities of Zn and Se in the solution were determined by gravimetric analysis[3]. The obtained results showed that the prepared ZnSe was a substantially stoichiometric compound and that any excess of Zn or Se was not precipitated with it.

* Part I (Zinc-Sulphide Phosphors) and Part II (Zinc-Sulphide: Selenide Phosphors (1)) of the investigations on this subject are reported in the references 2 and 1 cited in this paper respectively.

** The colon in this notation indicates variable proportion of the ingredients, so long as the total within the parenthesis is equal to one mole or stoichiometric proportion.

1) S. Asano: Jour. Appl. Phys. Japan, **23** (1954), 527.

2) S. Asano: Jour. Phys. Soc. Japan, **9** (1954), 580.

3) W, W. Scott: *Standard Methods of Chemical Analyses.* (D. Van Nostrand Co. N.Y. 1939) Vol. 1. pp 748, 1059.

The powders of pure ZnS and ZnSe were mixed thoroughly by milling in an agate-mortar with various mole proportions, and 2 g of purified KCl per 100 g of the mixture as flux and a small amount of chloride, nitrate or sulphate of Cu, Mn, Pb, Ag, or Bi as activator were added. This mixture was crystallized at 850°C for 20 min. or at 1100°C for 15 min. in pure N_2-atmosphere[4].

The concentration of the activator is represented by the weight percentage of the added activator-atoms.

2. Luminescence

On all the prepared phosphors the spectral-distribution curves of the luminescence excited by 3650 Å-line (Hg) were measured by a monochromator (GW-30. Shimadzu) and a multiplier (Mazda MS-9S), whose current was amplified by a dc amplifier consisting of a Mazda UX-54 tube and a Mazda High Resistance Tube (1Q18. $1.6\times10^8\Omega$). The current in the final stage was read by a micro-ammeter (Full scale: 20 μA). The spectral sensitivity of the multiplier fixed to the monochromator was calibrated by a rybon-filament tungsten lamp (Mazda Standard Lamp for Pyrometer. Brightness temperature: 2216°K)[5][6], and its linear respondency was ascertained by a Mazda Enlarging Lamp (100 V. 250 W.) for various wave-lengths as in the previous paper[2]. A high pressure mercury lamp with a ultra-violet (abbreviated as uv) filter (Mazda UVD-2) was used as the source of the excitant. The uv intensity was frequently measured by a photo-tube (Mazda PSV-50Y) showing a fair constancy of the source during the investigation.

The obtained results are shown in Figs. 1 and 2. In general, the peak wave-length gradually shifts towards longer wave-lengths with increasing proportion of ZnSe to reach finally to that of the orange or red-luminescent ZnSe phosphor as seen in the case of the phosphors prepared previously[1]. Mn-activated family* shows somewhat irregular shift in a similar manner to the case of the low crystallization temperature (850°C). With ZnS:Bi a green band is predominant when it is crystallized at 1100°C, while a blue luminescence predominates when crystallized at the low temperature. This green band shows a regular displacement with increasing proportion of ZnSe similar to the case of Cu-activated family. On the other hand the weak blue band disappears beyond a small proportion of ZnSe.

4) F. L. Audrieth: *Inorganic Syntheses.* (McGraw-Hill. N.Y. 1950 Vol. 3. p 17.

5) W. E. Forsyth: *Measurement of Radiant Energy.* (McGraw-Hill Co. N.Y. 1937) p 27.

6) L. S. Ornstein: Physica **3** (1936), 51.

* The family means a set of Zn(S:Se) phosphors, which are identical with respect to the sort and quantity of the added activator and the crystallization temperature.

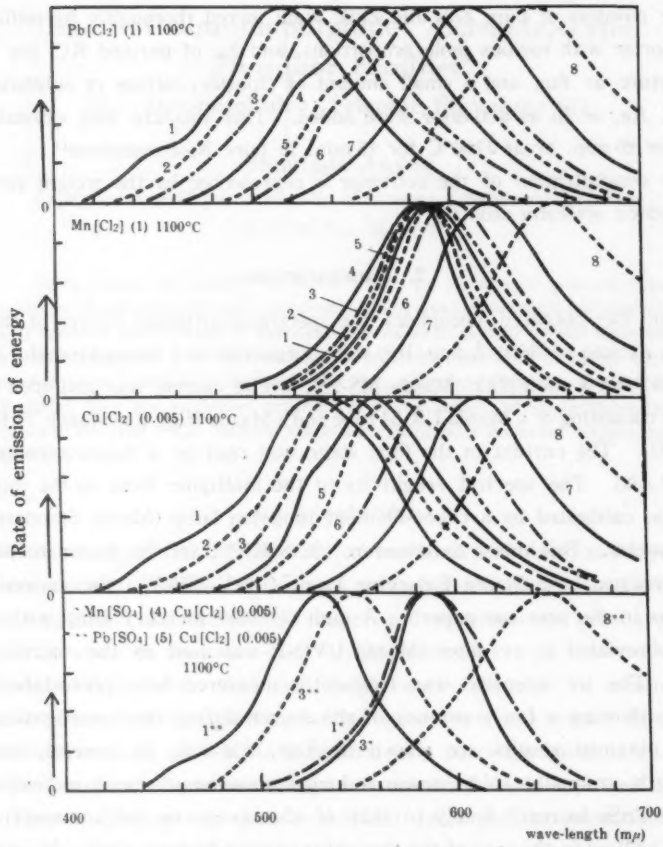

Fig. 1. Spectral-distribution curves of the luminescences excited by 3650 Å-line (Hg) at a room temperature.

Curve no. (1) ZnS (2) 9.5ZnS.0.5ZnSe (3) 9ZnS.ZnSe
(4) 8ZnS.2ZnSe (5) 7ZnS.3ZnSe (6) 5ZnS.5ZnSe
(7) 3ZnS.7ZnSe (8) ZnSe

3. Crystal Structure

It has been ascertained[1] that the mixture of ZnS and ZnSe forms a cubic solid-solution in any proportion as long as it is crystallized at 850°C. Further, diffraction patterns of the phosphors crystallized at 1100°C were photographed with an X-ray diffraction apparatus DX-60 (Shimadzu). Some of the photographs are shown in Fig. 3. For the crystallization temperature 1100°C, the predominant crystal structure tends to be hexagonal up to about 30 mole % of ZnSe

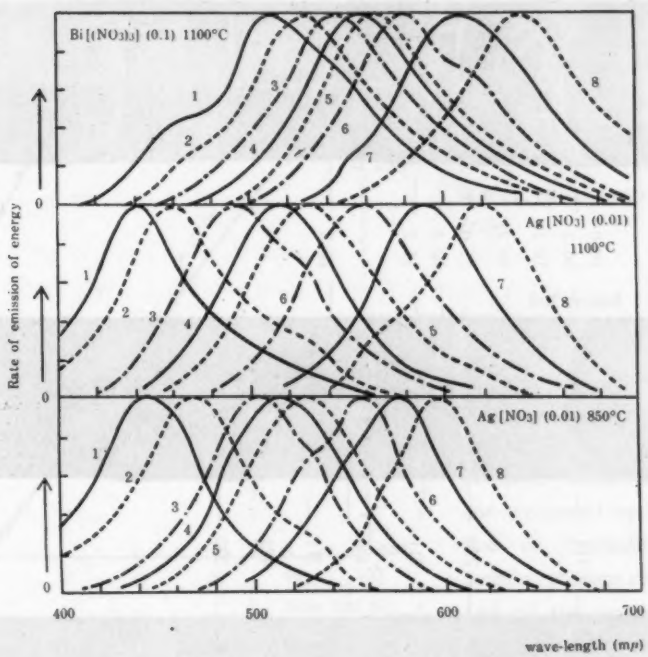

Fig. 2. Spectral-distribution curves of the luminescences excited by 3650 Å-line (Hg) at a room temperature.

The curve number corresponds to the host-crystal composition as in Fig. 1.

proportion, beyond which cubic structure predominates, irrespective of the sort of the added activator. The net planes (00, 2), (11, 0), (11, 2)....in hexagonal crystal corrsepond to the net planes (111), (220), (311)....in cubic crystal respectively as shown in Fig. 3.

Using the powder of pure cubic ZnS crystals (a_c=5.40Å) as standard to determine the camera-radius, the lattice constants of the inspected crystals were measured. The relation between the lattice constants and the proportion of ZnSe is shown in Fig. 4 in which the case of the low crystallization temperature is given for comparison. The lattice constants a and c of the hexagonal crystals and a_c of the cubic crystals increase linearly with increasing mole proportion of ZnSe in accordance with Vegard's law[7]. The axial ratios c/a of all the hexagonal crystals lie in the range from 1.63 to 1.64.

7) H. W. Leverentz: *Introduction to Luminescence of Solids.* (John-Wiley & Sons Co. N.Y. 1950) p 93.

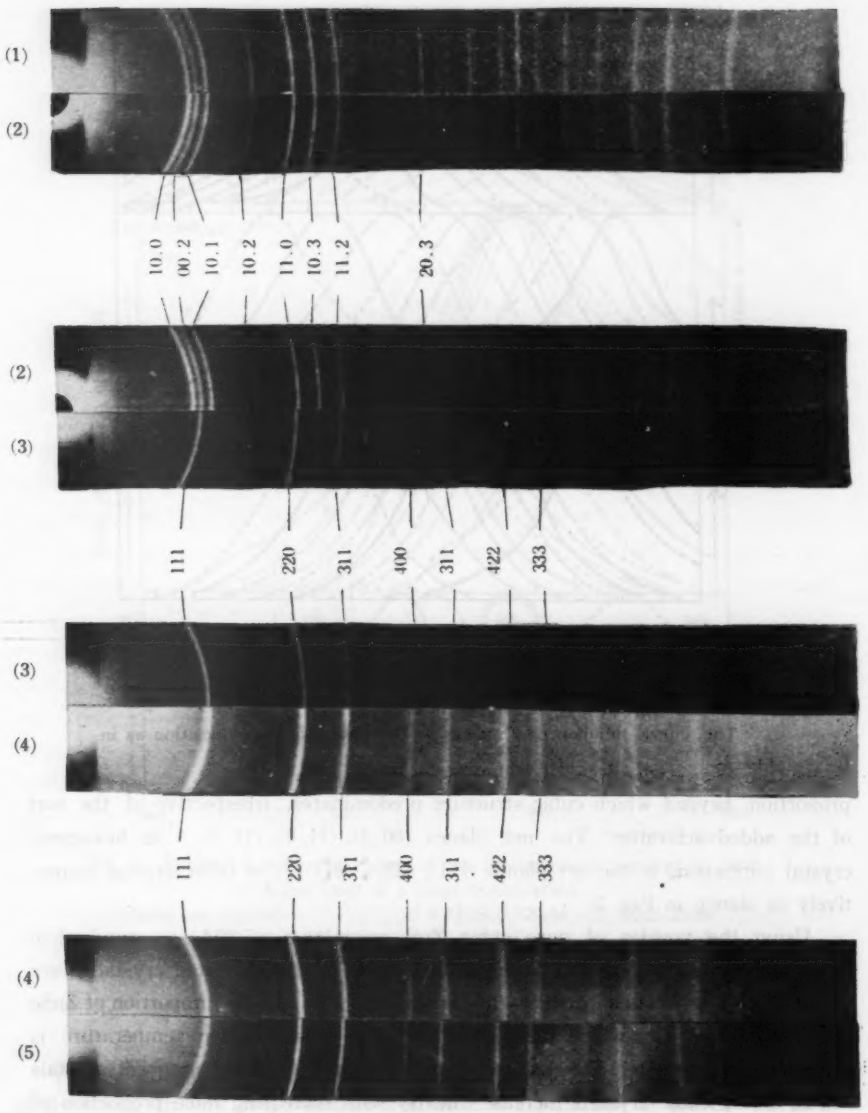

Fig. 3. X-ray diffraction patterns obtained at a room temperature.
Cu-K_α radiation, nickel filter.
1) ZnS:Bi (0.1) (2) 8ZnS.2ZnSe:Bi (0.1) (3) 7ZnS.3ZnSe:Bi (0.1)
(4) 5ZnS.5ZnSe:Bi (0.1) (5) ZnSe:Bi (0.1)
All the phosphors were crystallized at 1100°C.

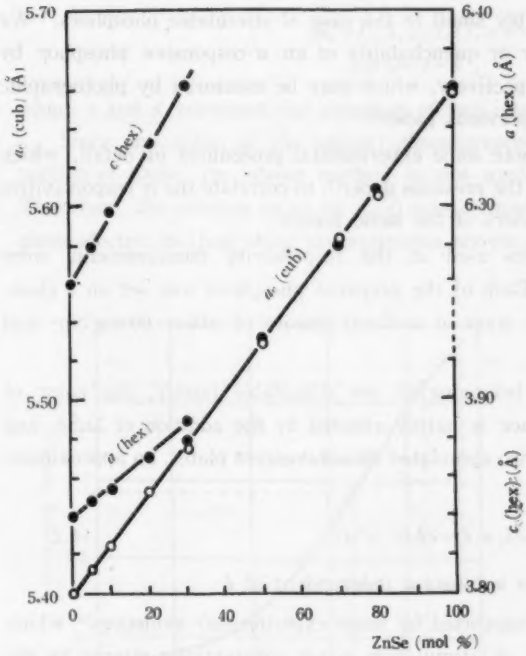

Fig. 4. Relation between lattice constants and the proportion of ZnSe.
Dots: Zn(S:Se):Bi[$(NO_3)_3$] (0.1) 1100°C
Circles: Zn(S:Se):Ag[NO_3] (0.01) 850°C.

The crystallographical relation[8]

$$a_c/a = \sqrt{3}\, c/2a ,$$

which holds in spharelite-wurzite transition, is also valid in the hexagonal and cubic Zn(S:Se) crystals containing equal proportion of ZnSe.

4. Infra-red Responsivity

(a) Method of Measurement.

Let $L_s(\lambda, x; t)$ and $L_q(\lambda, x; t)$ be the brilliances of the phosphor layer stimulated and weakened by ir irradiation of constant photon density (photons cm^{-2} sec^{-1}) and of the wave-length λ respectively, and $I_n(x; t)$ be that of natural phosphorescense, where x and t represent the mole proportion of ZnSe contained in the phosphor and the duration of ir irradiation respectively. The light sums L_s, L_q and L_n of these phosphorescences are then given by

$$L_s(\lambda, x) = \int_0^\infty I_s(\lambda, x; t)dt \qquad (4.1a)$$

$$L_q(\lambda, x) = \int_0^\infty I_q(\lambda, x; t)dt \qquad (4.1b)$$

and

$$L_n(x) = \int_0^\infty I_n(x; t)dt \qquad (4.1c)$$

respectively.

Further, the stimulated or quenched light-sum should be given by $L_s(\lambda, x)$ or $L_n(x) - L_q(\lambda, x)$ respectively, if the natural decay duration from the cessation

8) R. S. Mitchell et al: Amer. Mineral. **39** (1954), 773.

of preliminary uv excitation to the beginning of ir irradiation is made long enough for $L_n(x)$ to become neglegibly small in the case of stimulable phosphors. We have defined the stimulability or quenchability of an ir-responsive phosphor by $L_s(\lambda, x)$ or $L_n(x)-L_q(\lambda, x)$ respectively, which may be measured by photographic photometry as stated in the previous paper[2].

It is advisable here to quote some experimental procedures in detail, which are necessary, yet omitted in the previous paper[1], to correlate the ir responsivities one another of different members of the same family.

The phosphorescent plates used in the responsivity measurements were prepared by sedimentation. Each of the prepared phosphors was set on a glass-plate (0.5 mm in thickness) in layer of uniform density of about 60 mg/cm^2 and homogeneous screen texture.

Concerning the members belonging to one stimulable family, the color of the stimulated phosphorescence is hardly affected by the addition of ZnSe, and between the brilliances of the two stimulated phosphorescent plates, an approximate relation

$$I_s(\lambda, x; t)=cI_s(\lambda, x'; t) \tag{4.2}$$

is assumed to hold, where c is a constant independent of t.

This assumption may be supported by some experimental evidences[1] which suggest that the mechanism of stimulation is not substantially altered by the addition of ZnSe. Therefore, in this case the stimulabilities may be compared by means of the photographic method.

First, the obtained stimulability curves of the family members are so arranged that they correspond to a given photon-density by the graphical method[2]. Then the slit-width of the spectrograph (GW-30 Shimadzu) is so adjusted that, for a given wave-length λ_s, it gives the same photon-density, and the stimulation spectra of all the stimulable members are photographed on one plate (Fuji Panchro.) by using a weakening plate W. Under the same conditions, an intensity mark is then made on another part of the same plate by using the phosphorescent plate of the most stimulable member and a step-weakener W_s as described in the previous paper[2].

Interpolating the blackening densities $D_1, D_2 \cdots$ of the stimulation spectrograms for the wave-length λ_s on the characteristic curve C obtained for the same wave-length, the ratio M_s of the two stimulated light-sums can be determined. (cf. Fig. 5)

If Schwalzschild's relation can be assumed for the emulsion of the plate

used, from Eqs. (4.1a) and (4.2) M_s is given by[9]

$$M_s = L_s(\lambda, x)/L_s(\lambda, x') = Q \qquad (4.3)$$
$$\log Q = s - s' ,$$

where s and s' represent the abscissas of two interpolated points.

Since the color of the natural phosphorescence varies with increasing proportion of ZnSe, the above method is not applicable to quenchable families. Therefore, the relative value of $L_m(x)$ was estimated approximately by means of photo-electric method using the apparatus shown schematically in Fig. 6.

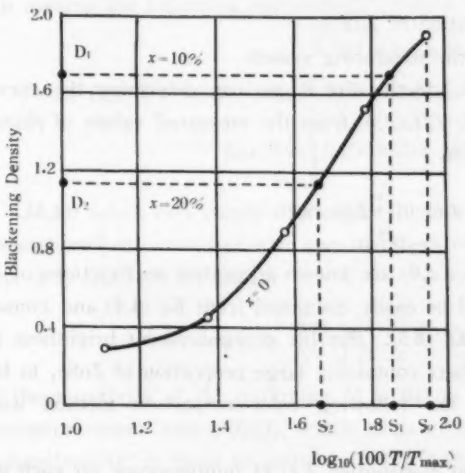

Fig. 5. Diagram illustrating the graphical method to determine the ratio M_s.
C: Characteristic curve of the plate.
T: Transmittance of the step-weakener W_s.
Sample: Zn(S:Se):Pb[SO_4](5):Cu(0.005) 1100°C
$t_n = 5$ min, $\lambda_s = 0.8\,\mu$

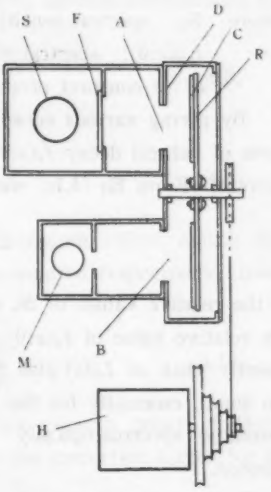

Fig. 6. Schematic diagram of the apparatus to measure the natural decay of phosphorescence.
A and B: Apertures
C: Phosphor layer
D: Diagram
F: uv filter (Mazda UVD-2)
H: Clockwork
M: Multiplier (Mazda MS-9S)
R: Rotative glass-disc
S: High pressure Hg-lamp

A uniform layer C of a phosphor to be measured is laid on the glass-disc R, which can be rotated with a desired speed by a clockwork H. A multiplier M (Mazda MS-9S), whose linear respondency has been ascertained, is placed in

9) P. Bauer: Zeits. f. Phys. **114** (1939), 245.

front of the aperture B of the diaphragm D and its photo-current is read by a sensitive galvanometer, while the phosphor layer C is excited through the aperture A.

If the disc R is rotated at angular velocity ω_0 which satisfies $t_n=\theta/\omega_0$ (t_n: natural decay duration in quenchability measurements. θ: angular distance between the two apertures.), then the photo-current $J(x)$ may be expressed in the form

$$J(x)=k\int S_\lambda I_{n\lambda}(x;0)d\lambda\ , \tag{4.4}$$

where S_λ: spectral sensitivity of the receptor

$I_{n\lambda}(x;0)$: spectral distribution of $I_n(x;0)$

k: a constant proper to the measuring system.

By giving various speeds ($<\omega_0$) to the disc R, we can determine the curve form of natural decay $\overline{I}_n(x;t)=I_n(x;t)/I_n(x;0)$ from the measured values of photo-current. From Eq (4.1c) we obtain

$$L_n(x)=I_n(x;0)\int_0^\infty \overline{I}_n(x;t)dt \tag{4.5}$$

If the relative values of S_λ and $I_{n\lambda}(x;0)$ are known accurately as functions of λ, the relative value of $I_n(x;0)$ would be easily computed from Eq (4.4) and consequently that of $L_n(x)$ also from Eq (4.5). But the phosphorescent brightness is too small, especially for the members containing large proportion of ZnSe, to be measured spectroscopically. So the following color-comparison method was adopted.

In the measurement of spectral distribution $I(\lambda)$ of luminescence on each of Zn(S:Se) phosphors, its relative peak output I_m and the photo-current J of the multiplier M *in situ* were measured simultaneously under the same experimental conditions. Then

$$J=k'I_m\int S_\lambda\overline{I}(\lambda)d\lambda \tag{4.6}$$

where $\overline{I}(\lambda)=I(\lambda)/I_m$

k': a constant proper to the measuring system.

The photo-current J_0 by a constant luminescent energy E from the phosphor should be given by

$$J_0=JE/I_m\int\overline{I}(\lambda)d\lambda \tag{4.7a}$$

which is, from Eq (4.6)

$$J_0 = k'E\int S_\lambda \bar{I}(\lambda)d\lambda \Big/ \int \bar{I}(\lambda)d\lambda \tag{4.7b}$$

The relative values of J_0 may be calculated from Eq (4.7a) for a set of some standard phosphors, whose peak wave-lengths lie side by side closely with one another all over the visible region from 440 to 650 mμ. Since we can assume that the phosphorescence band of Zn(S;Se) phosphor is also of nearly similar single-band-type as in the case of luminescence band (cf. Figs. 1 and 2), the degree of metamerism in spectral composition will be comparatively small[10] in the case where the luminescent color of a phosphor matches the phosphorescent color of another phosphor. Therefore, between the two spectral distributions we can assume the following approximate relation

$$k''I(\lambda) = I_{n\lambda}(x;0) \tag{4.8}$$

From Eqs (4.4), (4.7b) and (4.8) we obtain

$$I_n(x;0) = \int I_{n\lambda}(x;0)d\lambda = kk'EJ(x)/J_0 \tag{4.9}$$

If we select two standard phosphors, whose luminescent colors match the phorsphorescent colors of the two members to be compared respectively, from Eqs (4.5) and (4.9) we obtain

$$L_n(x)/L_n(x') = \left[\frac{J(x)}{J(x')}\right]\frac{J_0'}{J_0}\int_0^\infty \bar{I}(x;t)dt \Big/ \int_0^\infty \bar{I}(x';t)dt \tag{4.10}$$

If the sensitivity of the multiplier M is flat in the wave-length range of these phosphorescence bands, J_0'/J_0, which plays a part of the correction factor for its nonuniformity, is equal to unity. (cf. Eq (4.7b))

The ratio of the two quenched light-sums

$$M_q = [L_n(x) - L_q(\lambda, x)]/[L_n(x') - L_q(\lambda, x')] = \frac{L_n(x)}{L_n(x')}\left(1 - \frac{L_q(\lambda, x)}{L_n(x)}\right)\Big/\left(1 - \frac{L_q(\lambda, x')}{L_n(x')}\right), \tag{4.11}$$

may be evaluated by utilizing Eqs (4.7a) and (4.10) together with the values of $L_n(\lambda, x)/L_n(x)$ and $L_n(\lambda, x')/L_n(x')$ already known in the quenchability measurements[2].

The ir responsivities of the different members of the same family are thus correlated. The correlation is not strictly valid except in those cases where the different members to be compared have practically identical crystal-sizes, refractive indices and absorption coefficients for irradiated ir-ray. It is impossible in practice

10) M. G. Mellon: *Analytical Absorption Spectroscopy*. (John Wiley & Sons Co. N.Y. 1950) p 517.

to realize the complete color-matching and to be perfectly free from the metamerism. Therefore, the relative values of ir responsivities of the different members will not be very accurate.

(b) Experimental Results.

The general feature of the influence of ZnSe upon the ir responsivity of Zn(S:Se) phosphors crystallized at 1100°C is nearly similar to that upon those crystallized at 850°C notwithstanding the difference observed in crystal structure. Fig. 7 shows some photographs of stimulation and quenching spectra and Fig. 8 the ir-responsivity curves measured in the above manner. The ordinates of the

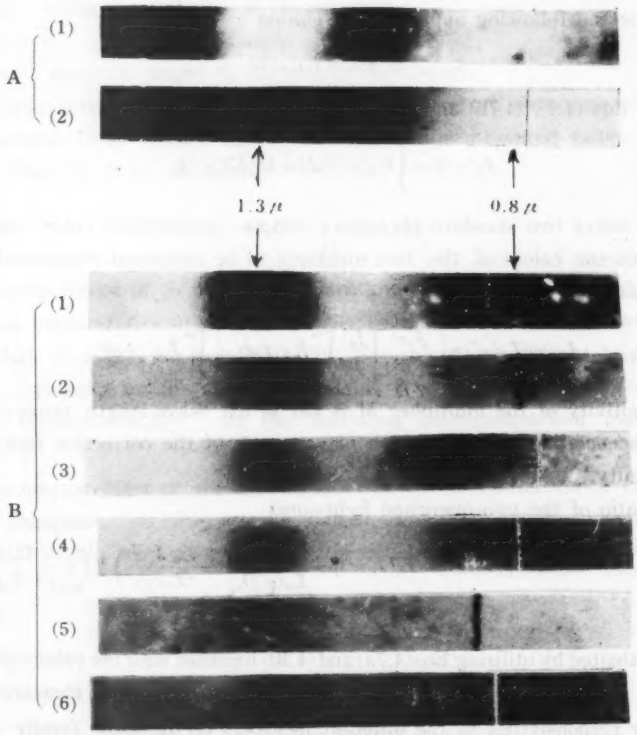

Fig. 7. Stimulation and quenching spectra of some Zn(S:Se) phosphors at a room temperature.

A (1) ZnS:Pb[SO_4](5):Cu(0.005) (2) 8ZnS.2ZnSe:Pb[SO_4](5):Cu(0.005)

B (1) ZnS:Cu(0.005) (2) 9.8ZnS.0.2ZnSe:Cu(0.005)

(3) 9.5ZnS.0.5ZnSe:Cu(0.005) (4) 9ZnS.ZnSe:Cu(0.005)

(5) 8ZnS.2ZnSe:Cu(0.005) (6) 7ZnS.3ZnSe:Cu(0.005)

All the phosphors were crystallized at 1100°C.

lined marks on the right side of each quenchability diagram in Fig. 8 indicate the relative values of $L_n(x)$ for each member, which were measured likewise.

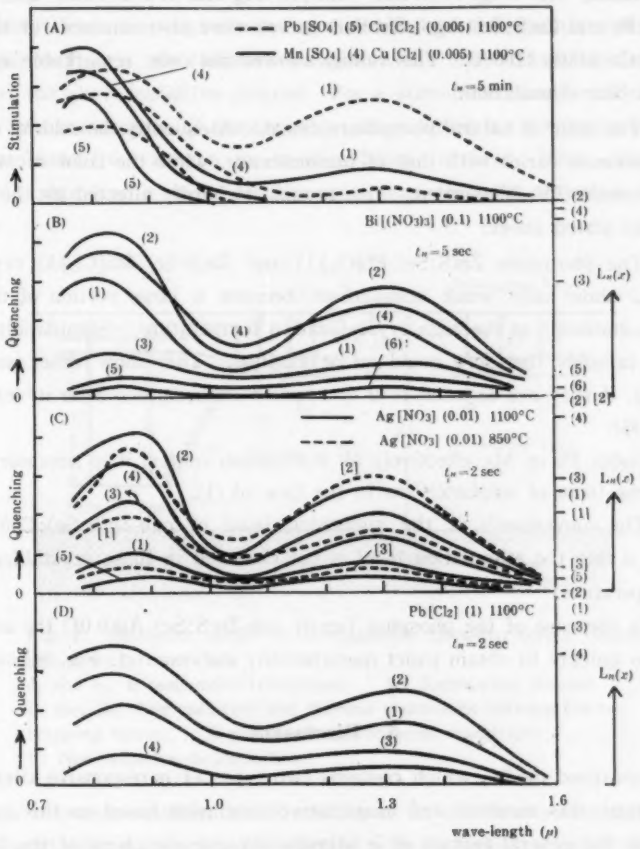

Fig. 8. Spectral ir-responsivity measured at a room temperature.
Curve no. (1) ZnS (2) 9.8ZnS.0.2ZnSe (3) 9.5ZnS.0.5ZnSe
(4) 9ZnS.ZnSe (5) 8ZnS.2ZnSe (6) 7ZnS.3ZnSe

(1) Of the two stimulation bands at about 0.8 μ and 1.3 μ, which may be observed[11] in hex-ZnS:Pb[SO_4]:Cu and hex-ZnS:Mn[SO_4]:Cu, the latter disappears at about 10% of and the former at about 30% of ZnSe proportion, their peak wave-lengths remaining unchanged. (cf. Figs. 7A and 8A)

(2) Both quenching bands at about 0.8 μ and 1.3 μ, which may be observed[11]

11) S. Asano: Jour. Appl. Phys. Japan, **22** (1953) 273.

in hex-ZnS:Cu, hex-ZnS:Bi and hex-ZnS:Ag, remain distinct until the after-glow loses its persistence at about 30% of ZnSe proportion so that it becomes visually unrecognizable. (cf. Fig. 7B) For example, Fig. 8B and C show the cases of Zn(S:Se):Bi and Zn(S:Se):Ag. Similar curves were also obtained for the family Zn(S:Se):Cu(0.005) 1100°C. This family showed not only remarkable quenching but weak blue stimulation.

(3) The color of natural phosphosrescence, consequently the color of quenched phosphorescence varies with that of luminescence, while the color of stimulated phsphorescence (Pb: blue-green. Mn: orange) is hardly affected by the addition of ZnSe as stated above.

(4) The phosphors Zn(S:Se):Pb[Cl_2](1) and Zn(S:Se):Mn[Cl_2](1) crystallized at 1100°C show only weak stimulation, because a large portion of the added chloride voltalizes[12] at the high crystallization temperature. Stimulability curves for these families, therefore, could not be obtained. They show rather remarkable quenching, if they are exposed to ir irradiation immediately after uv excitation. (cf. Fig. 8D)

To render Pb or Mn effectively as stimulation center, it is necessary to add them in the form of sulphate[13] as in the case of (1).

(5) The conversion[1] of the quenching band of cub-Zn(S:Se):Cu(0.005) at about 0.8 μ into the stimulation band is not observed in those crystallized at the high temperature.

(6) In the case of the phosphor family cub-Zn(S:Se):Ag(0.01) the after-glow decays too quickly to obtain exact quenchability curves. (cf. Fig. 8C)

5. Discussion

A generalized model, which contains two types of ir-responsive centers and isolated traps, was assumed and quantitative conclusion based on this model has shown that the general feature of ir stimulation and quenching of the Zn(S:Se)-type phosphors can be well explained[14]. By using this model the experimental results reported in the present paper may be explained as follows.

Fig. 9 shows the assumed model and the allowed electron transitions. An electron in an associated trap may pass over (or through) a potential barrier or be excited to an excition state by thermal activation and then be captured into an excited state of the emission center and finally recombine with the positive

12) H. W. Leverentz: ibid. p 72.
13) G. R. Fonda: J. Opt. Soc. Am. **36** (1946) 382.
14) S. Asano: Jour. Appl. Phys. Japan, **24** (1955) 57.

hole at its ground-state. (Transition B) In the latter case the associated trap may possibly be at many atomic-spacing distance from the parent emission center. The transition F is a non-radiative process which may occur in the manner similar to the above radiative process. For a stimulable phosphor the quantum efficiency of luminescence of the transition A, in which is concerned a conduction electron released from a trap by ir stimulation, is fairly large, while for a quenchable phosphor it is neglegibly small and then the transition A is non-radiative.

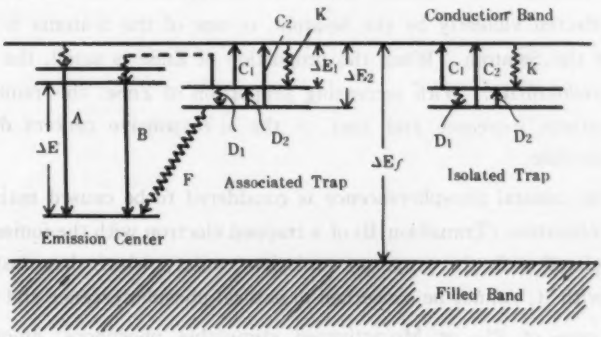

Fig. 9. Assumed model of ir-responsive phosphor-crystal showing allowed electron transitions.
c_1 and c_2: Ir-responsive transitions. K: Retrapping process.
D_1 and D_2: Non-radiative and thermal transitions between the two trapping states. A and B: Phosphorescent transitions.
F: Non-radiative de-excitation.

The ir-responsive center, which consists of an emission center and a double trap assoiated with it, is gradually affected with increasing number of the surrounding Se-atoms which substitutionally replace the S-atoms. Therefore, the energy intervals ΔE between the excited states and the ground-state at the emission center and the breadth of the forbidden band ΔE_f will vary with increasing proportion of ZnSe. On the other hand, according to the experimental results obtained above, it must be assumed that both the energy intervals ΔE_1 and ΔE_2 ($\Delta E_1 \fallingdotseq 0.95$eV. $\Delta E_2 \fallingdotseq 1.5$eV.) between the two trapping states and the bottom of the conduction band do not vary by the addition of ZnSe, until both the trapping states become affected too violently to remain stable.

If a Se-atom, which substitutionally replaces one of the S-atoms, is located as a non-ligand (that is, not a nearest-neighbor) of an ir-responsive center, the Se-atom may be expected to exert an indirect effect upon the energy intervals

ΔE at the emission center. The emission band of the phosphor then should exhibit a gradual displacement. But such an indirect, comparatively weak effect should be considered as unable to perturb the trapping states, which seem to be ascribable to a peculiar, tight binding of S- or (and) Zn-atoms. If a Se-atom is located as a ligand (combined nearest-neighbor) of an ir-responsive center, it may be expected to exert a direct effect upon both the emission center and the trap. Then the emission center will contribute to a new emission band which increases with increasing proportion of ZnSe and the associated trap will be destroyed, because the S-atoms, which are concerned in the constitution of the trap, are affected violently by the Se-atom, or one of the S-atoms is eventually replaced by the Se-atom. When the proportion of ZnSe is small, the non-ligated Se-atoms predominate. With increasing proportion of ZnSe, the number of the ligated Se-atoms increases and that of the ir-responsive centers decreases to become neglegible.

Since the natural phosphorescence is considered to be caused mainly by the direct recombination (Transition B) of a trapped electron with the ionized emission center associated with the trap, an emission center, which has lost the trap associated with it, cannot be concerned in natural phosphorescence and quenching.

In the case of Pb- or Mn-activated stimulable phosphors, among the ir-responsive centers only those which are hardly affected by Se-atoms may operate as the stimulation centers, the number of which decreases rapidly with increasing proportion of ZnSe. The remainder serve as the quenching centers and predominantly contribute to natural phosphorescence as stated above.

Though these centers are of stimulable type, the stimulation of the trapped electrons up to the conduction band by ir irradiation contributes not only to the phosphorescence but also to the quenching. The remarkable stimulation, therefore, cannot be observed when the concentration of the stimulable activator-atoms is weak. When it is excessively dense, it seems that considerable number of isolated emission centers or isolated double traps are formed additively. In order to explain the fact that the added ZnSe influences the two stimulation bands and quenching bands in the different manner as shown in Figs. 7 and 8, it is more reasonable to assume the formation of the isolated traps. The isolated double trap, which are in the two trapping states corresponding to the two stimulation bands, loses its upper state to become a single trap at about 10% of ZnSe proportion and finally the lower state also at about 30% of ZnSe proportion. The isolated traps formed in such a manner may cause the conspicuous stimulation even long after uv exitation.

In conclusion, the author wishes his sincere thanks to Dr. T. Harada and Dr. Y. Uehara of the Mazda-Laboratory (Tokyo-Sibaura Elec. Co.) for their helpful advice in performing this work. The author also is grateful to Prof. K. Asagoe who was so kind as to read the manuscript and offer useful suggestions.

On the Infrared-Responsive Behaviors of (Zinc: Cadmium-Sulphide: Selenide)-Type Phosphor Families.

IV. Zinc: Cadmium-Sulphide Phosphors

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(Received Feb. 21, 1955)

Some (Zn: Cd)S phosphor families activated with Pb, Mn, Cu, Bi or Ag have been prepared at two different crystallization temperatures, and their spectral infrared-responsivities and decay characteristics in natural and infrared-stimulated or -quenched phosphorescences are investigated under the same given conditions. The results are compared with those of the corresponding Zn(S: Se) phosphor families. The comparison shows that the influences of CdS and ZnSe upon the infrared-responsive behaviors of ZnS-type phosphors are substantially similar and that the model proposed in the previous paper is available also for the infrared-responsive (Zn: Cd)S phosphors.

1. Introduction

For some (Zn: Cd)S phosphors, results obtained on electric conductivity and photo-stimulation and -quenching of phosphorescence under infra-red (abbreviated as ir) irradiation have been reported fragmentally by several investigators[1]. The author prepared several (Zn: Cd)S phosphor families, which were activated with various metallic elements, and crystallized at 850°C or 1100°C. Their spectral ir-responsivities and the decay-characteristics of their ir-stimulated or -quenched phosphorescences were investigated systematically at a room temperature.

2. Preparation of Materials

Pure CdS powder was prepared by the following procedures. Into aqueous solution of $CdSO_4 8/3H_2O$ (Special-class reagent, Katayama Chemical Works, Japan) were added small amounts of pure $FeCl_3 6H_2O$ and pure H_2O_2, and also pure NH_4OH enough to obtain cadmium amine solution. After $Fe(OH)_3$ and

1) For example: A. E. Hardy: Trans. Electrochem. Soc. **87** (1945) 355 H. Kallmann et al: Phys. Rev. **37** (1952) 91.

occluded hydroxides of foreign metals were precipitated in the bottom of the vessel, the supernatant solution was separated by decantation and filtrated. $Cd(OH)_2$ could then be deposited from this solution by heating it on a sand-bath. These processes were repeated twice. The obtained $Cd(OH)_2$ was washed by decantation about twenty times with hot distilled water and dissolved in H_2SO_4 (30%) which had been distilled twice in silica-stills. The solution was evaporated under reduced pressure at a slightly lower temperature than 70°C. The evaporation was suspended before the deposited crystals of $CdSO_4 8/3H_2O$ amounted to about one third of the total obtainable upon calculation. These crystals were fractionally recrystallized twice in aqueous solution in a similar manner.

The obtained pure crystals were dissolved in distilled water again to a concentration of about 200 g/l. After the solution had been heated, stirred and electrolyzed between pure Pt-electrodes at 2.2 V for several days, was passed through it a slow stream of pure H_2S washed through several gas washing-bottles containing HCl, $Ba(OH)_2$ and distilled water. The supernatant solution was carefully decanted twice fractionally to segregate the discarded CdS (plus occluded low solubility sulphides). The decanted solution was diluted to about 10 g of $CdSO_4 8/3H_2O$ per litre to which 1 cc of pure conc. H_2SO_4 was added per 1 litre and then saturated with pure H_2S. Leaving it for one night, the supernatant solution was discarded by decantation. The remaining pure CdS was washed by decantation about fifty times with hot distilled water, separated by a glass-filter and finally dried at 110°C in an electric oven. Orange-yellow, homogeneous powder of pure CdS was thus prepared.

By spectroscopic analysis (with Shimadzu QF-60) the prepared CdS showed no detectable traces of foreign impurity-metals. In order to detect a trace, if any, of copper impurity in the CdS powder, the following extraction method was applied, which is capable of detecting μg-order of Cu-ions by photometric inspection[2].

By adding to each of 25 g lots of the CdS powder 0.025, 0.25, 2.5, 5.0, 10.0 and 15.0 μg of pure Cu ($CuSO_4 5H_2O$ purified by triple recrystallization) respectively, Cu-activated phosphors and, singly pure CdS phosphor were prepared at 850°C in N_2 -atmosphere. All these phosphors showed weak, red luminescence under ultra-violet (abbreviated as uv) excitation. For each one of them the following same procedure was applied.

Each 20 g of these phosphors is dissolved in hot pure conc. HNO_3. After removing the deposited sulphur by filtration, the filtrate is evaporated until the deposited solids appear dried. These solids are dissolved completely again in

2) E. Sudo: Jour. Chem. Soc. Japan **72** (1951) 718.

300 cc of distilled water and 10 cc of aqueous solution (20%) of purified AcO(NH_4) is added to it as buffer. The pH of the solution is made equal to 3 accurately by adding pure AcOH, and 1 cc of acetic-acid solution (2%) of pure oxine (8-hydroxy-quinoline) is mixed with it. The mixed solution is led into a separation funnel with 20 cc of pure chloroform, and by shaking the funnel sufficiently, the chloroform layer is separated. By filtrating the separated chloroform through a dried filter-paper, the water droplets making it turbid may be removed and then clear liquid is obtained.

20 cc of chloroform, thus obtained for every CdS phosphor, in which Cu-oxinate is present in varying concentrations, is led into a Baly's tube (5 cm in length). By using a monochromator (Shimadzu GW-30) and a Mazda Multiplier MS-9S, the relation between the absorbancy coefficient and the added Cu-amount is determined at the wave-length 530 mμ, in whose vicinity the spectral transmittance of the chloroform solution of Cu-oxinate is nearly flat and the sensitivity of the receptor is comparatively high. The measured relation obeyed approximately to Beer's law in the Cu-amount range from 2.5 μg to 15.0 μg. But the among the transmittancies for the cases of 0.25, 0.025 μg and the pure phosphor any difference could not be detected. To avoid accidental errors, the experiments were repeated twice but the same results were obtained.

From the above results the Cu-amount in the prepared CdS powder was estimated to be $<10^{-5}$%, which cannot affect the optical properties of the furnished phosphors.

Since chloroform solutions of oxinate of other metals Fe, Bi, Al and Ni, which may be effectively extracted with the pH value 3, have also nearly similar absorbancy-concentration curves to that of Cu-oxinate within the concentration range from 1 to 10 μg per 10 cc of chloroform[3], the above order-estimation may be roughly valid for these metals which may be contained in the prepared CdS.

The pure ZnS powder, which had been prepared through careful procedures and whose Cu-impurity amount also had been estimated to be less than 10^{-5}%[4], was used as the partner ingredient. The powders of ZnS and CdS mixed thoroughly with various mole proportions, being milled in an agate-mortar. To the mixture were added 2 weight percents of pure KCl as flux and a small amount of chloride or nitrate of Pb, Mn, Bi, Cu or Ag as activator. The mixture was put on a silica-boat and crystallized at 850°C for 20 min. or at 1100°C for 15 min. in pure N_2-atmosphere[5]. The concentration of the activator is represented by weight-percentage of the added activator-atoms.

3) T. Moellor: Ind. Eng. Chem. Anal. Ed. **15** (1943) 346.
4) S. Asano: Jour. Phys. Soc. Japan **9** (1954) 580.
5) L. F. Audrieth: *Inorganic Syntheses* (McGraw-Hill Co. N. Y. 1950) Vol. 3. p 17.

3. Luminescence and Crystal Structure

Hitherto the luminescence and crystal structure of (Zn: Cd)S phosphors, especially Cu- and Ag-activated phosphor families have already been studied by many investigators. The author studied, however, the luminescence and crystal structure of some of the prepared phosphors in order to inspect the deviation of their optical and crystallographical properties from the typical normality. The deviation may occur by oxidation, fluctuation of temperature, contamination from silica-wall and other unexpected causes during crystallization.

Spectral-distribution curves of the luminescences excited by 3650 Å-line (Hg) at a room temperature were measured by using the monochromator (Shimadzu GW-30) and the Mazda Multiplier MS-9S, whose photo-current was amplified by

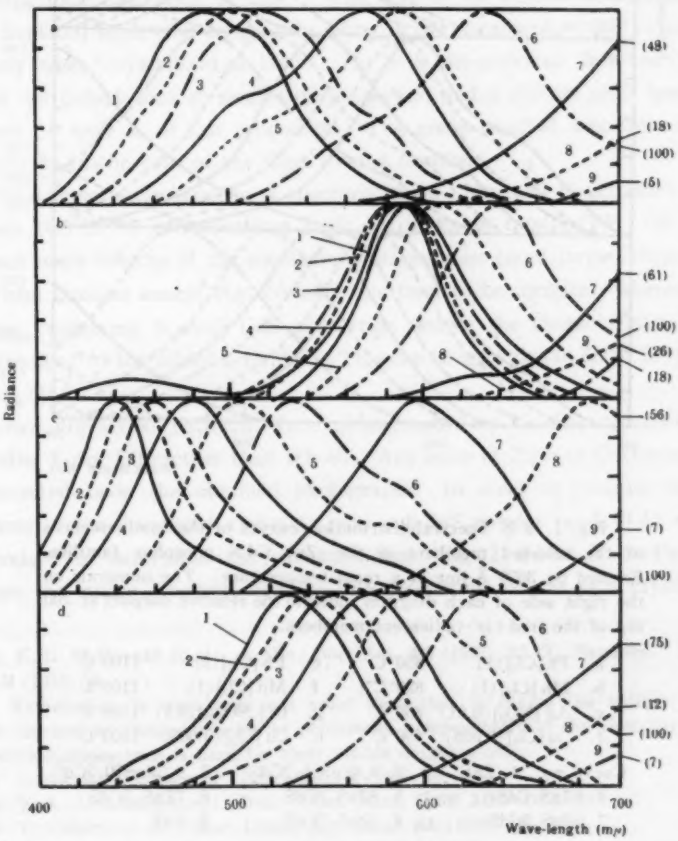

Fig. 1-a.—d.

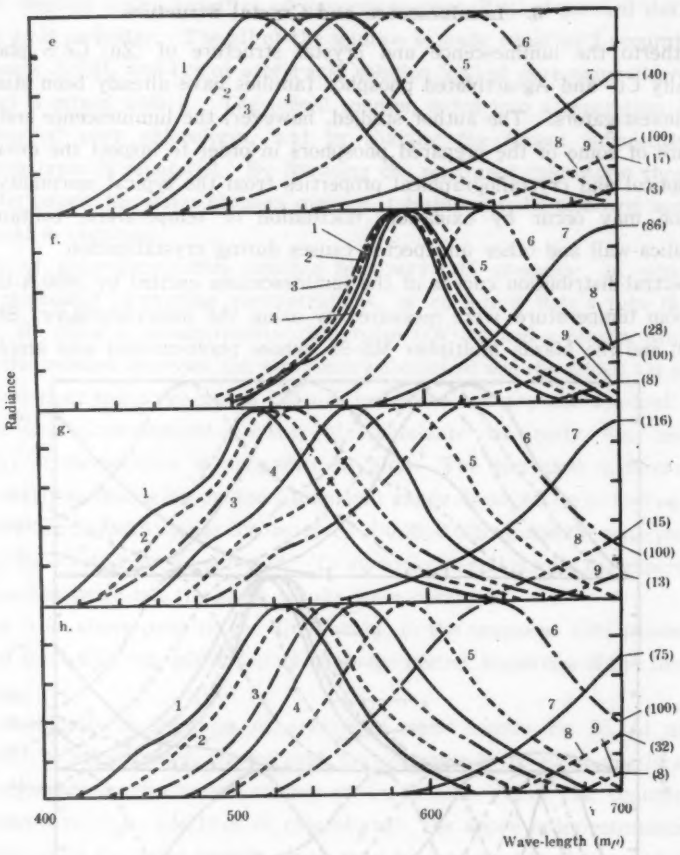

Fig. 1. a–h. Spectral-distribution curves of the luminescences of the selected members in the (Zn: Cd)S phosphor families. Excited by 3650 Å-line at a room temperature. The numerals on the right side of each diagram indicate the relative outputs at 700 mμ of the (red+ir)-radiescent members.

a.	Pb $[Cl_2]$ (1)	850°C	e.	Pb $[Cl_2]$ (1)	1100°C
b.	Mn $[Cl_2]$ (1)	850°C	f.	Mn $[Cl_2]$ (1)	1100°C
c.	Ag $[NO_3]$ (0.01)	850°C	g.	Bi $[(NO_3)_3]$ (0.1)	1100°C
d.	Cu $[Cl_2]$ (0.005)	850°C	h.	Cu $[Cl_2]$ (0.005)	1100°C

Curve no. 1. ZnS	2. 9.8ZnS.0.2CdS	3. 9.5ZnS.0.5CdS
4. 9ZnS.CdS	5. 8ZnS.2CdS	6. 7ZnS.3CdS
7. 5ZnS.5CdS	8. 3ZnS.7CdS	9. CdS

a dc amplifier[6] connected to a micro-ammeter (Full scale 50 μA). The linearity between the light intensity and the final response was ascertained at various wave-lengths. The spectral sensitivity of the receptor through the monochromator was calibrated as stated in the previous paper[7].

The obtained results are shown in Fig. 1. The well-known general feature that the peak wave-length in one phosphor family is displaced towards longer wave-lengths with increasing proportion of CdS and that it reaches finally to that of the red- plus ir-radiescent* CdS phosphor[8], is seen in all the prepared families.

The typical cases of the regular displacement are observed in the Cu- and Ag-activated families, where the peak wave-length shifts nearly linearly with increasing mole proportion of CdS[9]. The peak in the Pb-activated family tends to be displaced somewhat irregularly when it is crystallized at 850°C, but nearly regularly when crystallized at 1100°C. In both Mn-activated families the peak-shift is not conspicuous at small CdS proportion and a definite shift begins first at about 10 mole % of Cds proportion. The green band of hex-ZnS: Bi shifts regularly as in the case of the Cu-activated families.

These remarkable tendencies observed in Pb-, Mn- and Bi-activated families are seen also in the corresponding Zn(S: Se) phosphor families[7][10]. In general, the peak wave-lengths of the members containing an equal large CdS proportion in various families except Ag-activated one tend to be identical, whereas every member containing a small CdS proportion shows the characteristic emission band peculiar to the added activator. This can be seen also in Zn(S: Se) phosphor families[7][10].

X-ray diffraction patterns were photographed by Cu-$K\alpha$ radiation with a Shimadzu X-ray Diffraction Unit DX-60. Any trace of ZnO- or CdO-crystals was not detected upon the obtained photographs. In order to measure the lattice constants of the inspected crystals, pure cub-ZnS powder (a=5.40 Å) was used as standard to determine the camera-radius. Fig. 2 shows Vegard's relation between the lattice constants and the CdS proportion for the two crystallization

6) K. L. McDonald et al: J. Opt. Soc. Am. **42** (1952) 321 T. Namioka. Science of Light **3** (1954) 15.

* Radiescence is used here in a broad sense that it covers the visible and near-visible (uv and ir) photon-emission of phosphors, independently of the visibility by human eye, while luminescence is used for their visible emission only.

7) S. Asano: Science of Light (1955) **4** (1955) 16.

8) V. A. Arhangeliskaya: Dokl. Akad. Nauk SSSR **100** (1955) 233.

9) Y. Uehara et al: Jour. Chem. Soc. Japan **61** (1940) 405, 553.

10) S. Asano: Jour. Appl. Phys. Japan **23** (1954) 527.

temperatures. The axial ratio c/a in the hexagonal crystals lie in the range from 1.63 to 1.64. Even in the case of the low crystallization temperature (850°C) the predominant crystal structure tends to be hexagonal by the addition of only several mole percents of CdS, regardless of the kind of added activator.

The above inspections on the luminescence and crystal structure show that the prepared phosphors may be considered to have the normal optical properties.

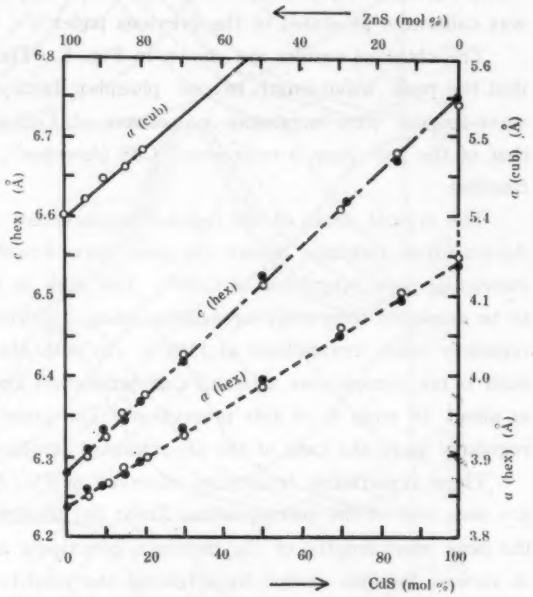

Fig. 2. Relation between the lattice constants and the CdS proportion at a room temperature.
Dots: (Zn: Cd)S: Cu(0.005) 1100°C
Circles: (Zn: Cd)S: Ag(0.01) 850°C
Into all the phosphors 2 weight % of KCl was added as flux.

4. Spectral Irresponsivity

By the procedures similar to those in the previous papers[4)7)], spectral ir-responsivities of the prepared phosphors were measured and those of the different members belonging to the same family were correlated one another.

Several typical examples showing the influence of the added CdS upon the irresponsivity are given in Fig. 3. In general, the two stimulation and quenching bands found at about 0.8 μ and 1.3 μ remain distinct showing no displacement of their peak wave-lengths until the after-glow loses its persistence visually at about 40 mole percents of CdS proportion. The color of the stimulated phosphorescence (Pb: blue-green. Mn: orange) in one family is hardly affected by the addition of CdS, while that of the natural phosphorescence, consequently that of the quenched one varies with the color of luminescence.

Pb- and Mn-activated families crystallized at 850°C show remarkable stimulation but those crystallized at 1100°C more quenching than stimulation

which is weak. (cf. Fig. 3 a and b), as in the corresponding Zn(S: Se) phosphor families[7)10)]. The Ag-, Cu- and Bi-activated families show not only remarkable

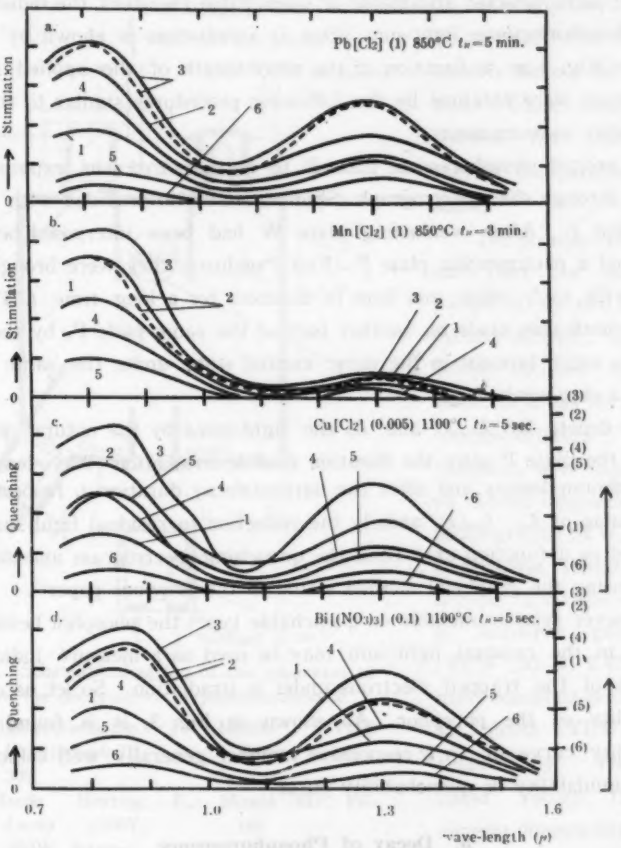

Fig. 3. a–d. Spectral infrared-responsivity curves measured at a room temperature.

Curve no. 1. ZnS 2. 9.8ZnS.0.2CdS 3. 9.5ZnS.0.5CdS
4. 9ZnS.CdS 5. 8ZnS.2CdS 6. 7ZnS.3CdS

t_n: natural-decay duration before ir irradiation.

The ordinate of the lined mark on the right side of each quenchability diagram indicates the relative value of the natural-phosphorescence light-sum of each member. Dotted curves show the exhaustibility curves of the corresponding members. (t_i=3 min.)

quenching but the members containing 2 to 10 mole % of CdS in particular show also weak stimulation in the beginning instant of ir irradiation. (cf. Fig. 6 c)

Two of the similar quenchability-characteristics of these four quenchable families are shown in Figs. 3 c and d.

About some selected stimulable or quenchable members, the reduction in the natural-phosphorescence light-sum after ir irradiation is shown by the dotted curves in Fig. 3 as a function of the wave-length of the applied irradiation. These curves were obtained by the following procedures similar to those in the quenchability measurements.

The excited phosphorescent plate P to be measured was exposed to ir irradiation through the spectrograph (Shimadzu GW-30) provided with a step-slit for duration t_i. After weakening plate W had been interposed between the plate P and a photographic plate P_1 (Fuji Panchro.), they were brought in close contact with each other, and kept in darkness for a long time t. Further, an intensity mark was made on another part of the same plate P_1 by the plate P, which was again brought in the same excited state, under the same conditions by using a step-weakener W_s.

If we denote by $L_{in}(\lambda)$ and L_n the light-sums by the natural phosphorescence of the plate P after the duration t_i of ir irradiation (Wave-length: λ) of constant photon-density and after the natural-decay duration t_i respectively, the relative value of $L_n - L_{in}(\lambda)$, namely the reduction in residual light-sum may be determined as a function of λ from the quenching-spectrogram and the intensity mark by using the graphical method stated in the previous paper[4].

Whichever type (stimulable or quenchable type) the phosphor belongs to, the reduction in the residual light-sum may be used as a measure indicating the exhaustion of the trapped electrons under ir irradiation. So let us call it the exhaustibility of the phosphor. As shown in Fig. 3, it is found that the exhaustibility curve of an ir-responsive member generally well coincides with its own stimulability or quenchability curve.

5. Decay of Phosphorescence

(a) Measuring Apparatus

The decay-curves of the natural phosphorescence and the ir-stimulated or -quenched phosphorescence of the prepared phosphors were measured by the apparatus schematically shown in Fig. 4. A Mazda Heating Lamp (100V. 250W-S-type. Color temperature: 2060°C), enclosed in a light-tight, water-cooled container provided with a Mazda IRD-1 Filter, was used as the ir source, It was lighted with a voltage stabilizer. A high pressure mercury lamp (Mazda HL-300) with a Mazda UVD-2 Filter was used as the source of excitant. A thick layer of the phosphor to be measured was prepared on a glass-disc (5 cm in diameter).

The sample was mounted on a table in a light-tight box. The ir irradiance incident upon the sample was measured by a calibrated thermocouple[4] and the uv intensity by a Mazda Photo-tube PSV-50 Y frequently during the investigation. These measurements showed that the sources stayed comparatively constant.

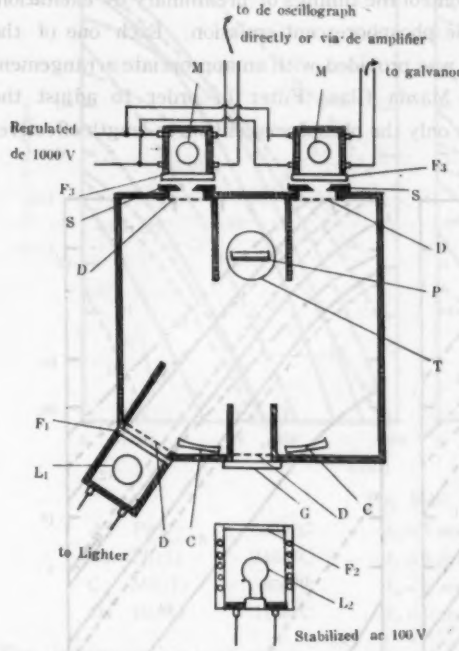

Fig. 4. Schematic diagram of the apparatus to measure the decay-curve of phosphorescence.

L_1:	High pressure Hg-lamp (Mazda HL-300	F_1:	Mazda UVD-2 Filter
L_2:	Mazda Heating Lamp (100V. 250W. S-type)	F_2:	Mazda IRD-1 Filter
M:	Mazda Multiplier MS-9S	F_3:	Mazda Glass Filter
C:	Al-coated concave-mirror	S:	Variable slit
P:	Sample	G:	Opal-glass plate
T:	Table to mount the sample	D:	Shutter

The phosphorescent emission from the sample was picked up by two multipliers (Mazda MS-9S), the sample being focused upon their sensitive areas by Al-coated concave-mirrors. These two receptors were connected to an electro-magnetic type dc oscillograph (YEW. N-3) with a sensitive vibrator (YEW. D-type. 1.5 μA/mm) and to a sensitive galvanometer (YEW. D3-A. 2.43×10^{-10} A/mm) equipped with a universal shunt (YEW. GS-1A) respectively. The former could record the quick current-change during 2 to 15 sec. immediately after the ceasing of uv excitation or the beginning of ir irradiation and the latter the slow current-change following it. The galvanometer-terminals were shunted by a resistance of 16,000Ω for critical damping within all available current-ranges. If necessary, the current from the former receptor could be amplified by a dc amplifier[11] consisting of a Mazda UX-54 tube and a Mazda

11) L. A. Dubridge et al: Rev. Scient. Instr. **4** (1933) 532.

High Resistance Tube (1Q18. $1.6\times10^{8}\Omega$).

A shutter was fixed in front of each one of the four apertures of the box enclosing the sample in order to control the timings of preliminary uv excitation, ir irradiation and reception of the phosphorescent emission. Each one of the apertures of the receptor containers was provided with an appropriate arrangement for holding a variable slit and a Mazda Glass Filter in order to adjust the incident light-quantity and to make only the phosphorescent wave-length effective.

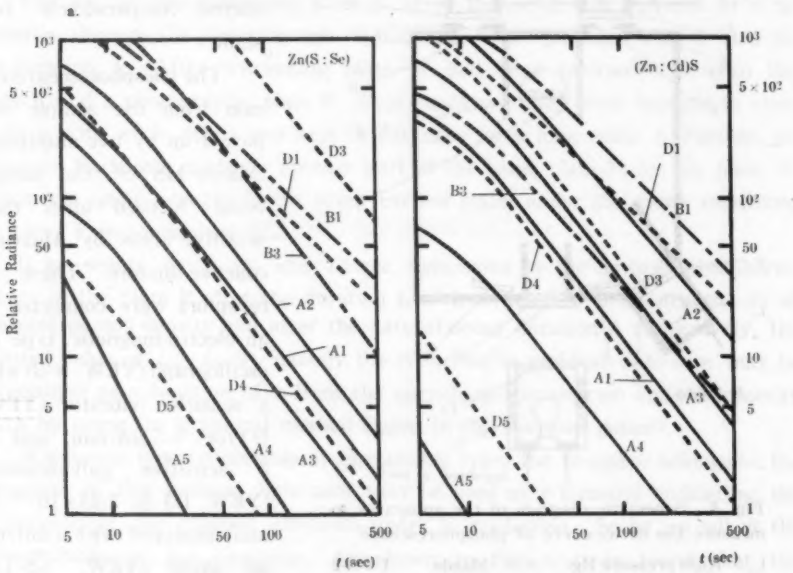

Fig. 5-a. Log-log plots of the decay-curves of natural phosphorescences (a) and ir-stimulated or -quenched phosphorescences (b). Thick layer, measured from the excited or irradiated side at a room temperature.

Curve no.	1	2	3	4	5
CdS or ZnSe (mole %)	0	5	10	20	30

uv excitation: Mazda HL-300+Mazda UVD-2 Filter, distance at 30 cm for 3 min.
ir irradiation: Mazda Heating Lamp (100V. 250W. S-type)+Mazda IRD-1 Filter.
ir irradiance: 3.0m W/cm².
t: time after the cessation of uv excitation.
t_n: natural-decay duration before ir irradiation.
t_i: time after the beginning of ir irradiation.

A: Pb(1) 850°C
B: Pb(1) 1100°C
D: Bi(0.1) 1100°C

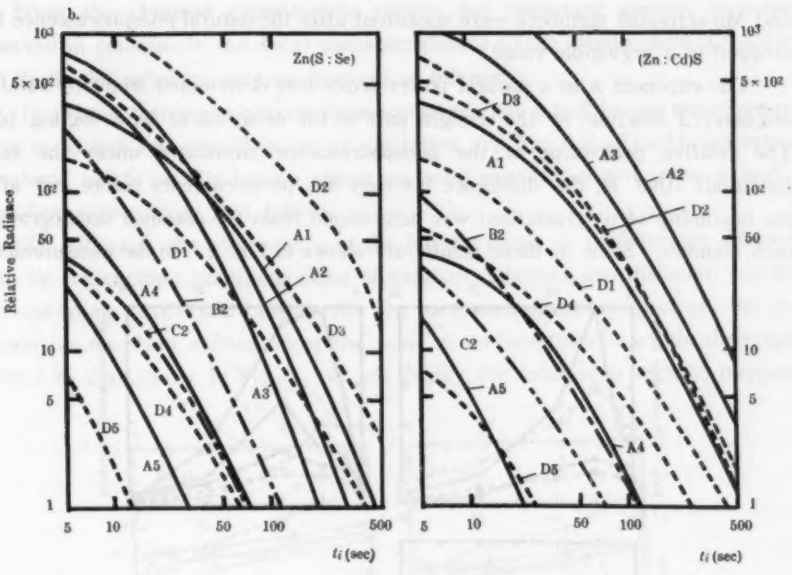

Fig. 5–b.

A :	Pb(1)	850°C	t_n=3 min.	Stimulated phosphorescence
B :	Pb(1)	1100°C	t_n=3 min.	Stimulated phosphorescence
C :	Mn(1)	850°C	t_n=1 min.	Stimulated phosphorescence
D :	Bi(0.1)	1100°C	t_n=5 sec.	Quenched phosphorescence

The ir source was placed in a position for the ir-rays to fall on the sample surface at nearly normal incidence. The zero-points in the natural-decay and the ir stimulated or -quenched decay were determined by the readings at the time when the sample was dismounted and when it was thoroughly quenched out after prolonged ir-irradiation respectively.

The two decay-curves measured simultaneously by the oscillograph and the galvanometer on one phosphor were jointed in a log-log diagram by fitting them in the overlapped decay-range. The relative radiances of the phosphorescences of the fellow-members in the same family were compared one another by the color-comparison method stated in the previous paper[7].

(b) Experimental Results.

For all the ir-responsive members the decay-curves of their natural-phosphorescences and those of their ir-stimulated and -quenched phosphorescences were measured under the same conditions. Some of the obtained results are shown in Fig. 5. The decay-curves of the ir-stimulated phosphorescences of Pb-

and Mn-activated members were measured after the natural phosphorescence had dropped to a neglegible value.

The exponent n in a natural power-decay was determined from the ratio (Δ ordinate)/(Δ abscissa) in the straight part of the decay-curve on a log-log plot. The relative peak-value of the phosphorescence stimulated under the same conditions (that is, the difference between the photo-currents before and after the beginning of ir irradiation) was determined from the obtained oscillogram of each member. Some of these results are shown in Fig. 6. In the measurements

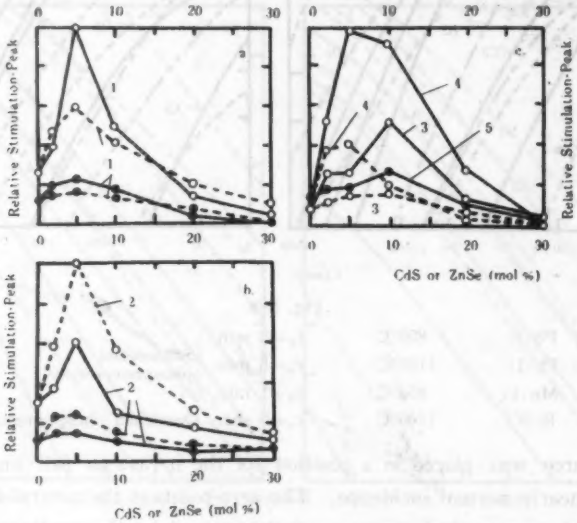

Fig. 6. Relation between the stimulation-peak and the foreign-ingredient proportion at a room temperature. Measured under the same exciting and irradiating conditions as in Fig. 5.

Curve no. 1.	Pb $[Cl_2]$ (1)	$t_n = 1$ min.
2.	Mn $[Cl_2]$ (1)	$t_n = 30$ sec.
3.	Cu $[Cl_2]$ (0.005)	$t_n = 15$ sec.
4.	Ag $[NO_3]$ (0.01)	$t_n = 15$ sec.
5.	Bi $[(NO_3)_3]$ (0.1)	$t_n = 15$ sec.

Dots: crystallized at 1100°C. Circles: cristallized at 850°C.
Real lines: (Zn : Cd)S Dotted lines: Zn(S : Se)

for Ag-, Cu- and Bi- activated members in which the peak-values were very small, the photo-currents were amplified by the dc amplifier[11]. Since the color of the stimulated phosphorescence in one family is hardly affected by the addition of CdS or ZnSe as stated previously, the peak-values of the fellow-members in the same family may be considered as nearly proportional to the initial radiances of their own stimulated phosphorescences.

From the obtained experimental results the important general features observed in common in the decay-characteristics of all the ir-responsive (Zn: Cd)S and Zn(S: Se) members may be itemized as follows:

(1) The ir-responsive natural-phosphorescence has a well-known power-decay form at least a few seconds after uv excitation. (cf. Fig. 5 a) The Mn-activated members, which initially have a strong decaying exponential-part, show a fairly presistent power-decay that follows.

(2) Although the exponent n in the natural decay is considerably affected both by the exciting conditions (kind of excitant, intensity and duration) and by the operating temperature even with one particular phosphor, n of all the ir-responsive members excited under the same given conditions lie within the range from 1 to 2 as shown in Fig. 7. In one family the value of n tends to increase

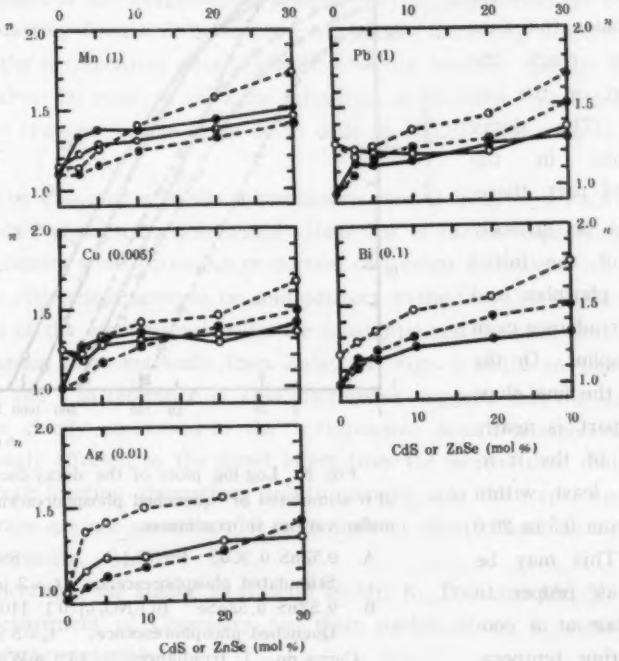

Fig. 7. Dependence of the exponent n in ir-responsive natural-decay upon the foreign-ingredient proportion at room temperature. Measured under the same exciting conditions as in Fig. 5.

Dots: crystallized at 1100°C. Circles: crystallized at 850°C
Real lines: (Zn: Cd)S Dotted lines: Zn(S: Se)

with increasing proportion of foreign ingredient (Cds or ZnSe), especially in the Zn(S: Se) phosphor families crystallized at 850°c.

(3) The exponents n of Pb-, Bi- and Cu-activated cub-ZnS phosphors crystallized at 850°C are somewhat larger than those of the corresponding hex-ZnS phosphors crystallized at 1100°C. In the Ag- and Mn- activated ZnS phosphors this dissimilarity is not so conspicuous. (cf. Fig. 7)

(4) ir-stimulated or -quenched decay-curves on a log-log plot has a nearly straight part for prolonged ir irradiation. Its slope approaches to a constant value of about−2 with increasing irradiation time, independently of the foreign ingredient proportion. (Fig. 5 b) As shown in Fig. 8, the more intense the applied irradiance is, the longer becomes the time required to reach the straight part on the log-log plot. The decay characteristics in the initial curved part, therefore, should be strongly dependent of the initial state of the phosphor and the applied irradiance even for one phosphor. On the other hand, the final slope in the tail-part is nearly independent of the ir irradiance at least within the range from 0.5 to 20.0 mW/cm². This may be considered as proper to each phosphor at a constant operating temperature.

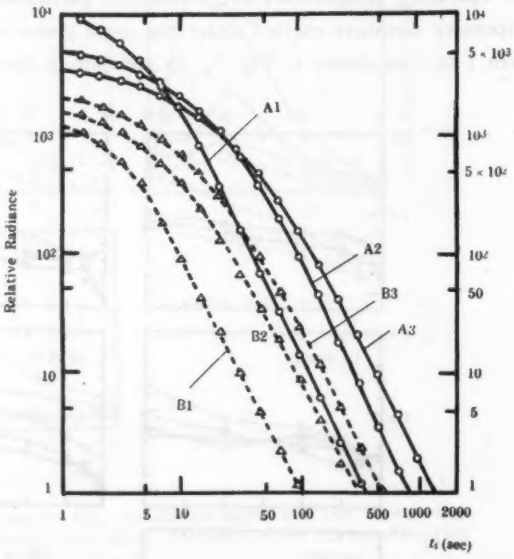

Fig. 8. Log-log plots of the decay-curves of ir-stimulated or -quenched phosphorescences under various ir irradiances.

A. 9.5ZnS.0.5CdS: Pb [Cl_2] (1) 850°C
Stimulated phosphorescence. t_n=3 min.
B. 9.5ZnS.0.5ZnSe: Bi [$(NO_3)_3$] (0.1) 1100°C
Quenched phosphorescence. t_n=5 sec.
Curve no. 1. Irradiance 13.5 mW/cm²
2. 〃 2.5 〃
3. 〃 1.0 〃

(5) In reference to Figs. 3, 5, and 6, the radiances and the durations of the ir-responsive natural-phosphorescence and of the ir-stimulated phosphorescence increase by mixing several mole percents of foreign ingredient, when compared with the ZnS

phosphor of the same family. This increase in phosphorescence-radiance is conspicuous particularly in the families crystallized at 850°C. Beyond this optimum proportion they decrease again rapidly because of the diminuation in initial radiance and, especially in natural phosphorescence, because of increasing n value.

6. Summary

The influence of CdS upon the ir-responsive behaviors of ZnS phosphors are qualitatively similar to that of ZnSe. The model proposed in the previous paper[7] for the explanation of the ir-responsive phenomena of Zn(S: Se) phosphors, therefore, is also available for the (Zn: Gd)S phosphor families.

The remarkable quantitative differences between the phosphorescence characteristics of the two phosphor-systems may be summarized as follows:

(1) Starting from a ZnS phosphor and adding increasing proportion of CdS or ZnSe, the ir-responsive natural-phosphorescence becomes visually unrecognizable at about 30 mole % of ZnSe proportion in Zn(S: Se) phosphor families, whereas it remains visible up to 40–45 mole % of CdS proportion in (Zn: Cp)S families.

(2) The exponent n in the ir-responsive natural-decay of a Zn(S: Se) phosphor family increases more remakably than that of the corresponding (Zn: Cd)S phosphor family with increasing proportion of foreign ingredient. (cf. Fig. 7)

These differences seem to be contradictory to the fact that CdS promotes the elongation of the atomic-spacing (lattice constants) and the peak-shift in luminescence emission more markedly than ZnSe. (cf. Figs. 1 and 2 in this paper and Figs. 1, 2 and 4 in reference 7) This discrepancy suggests that the shallow traps which are chiefly concerned in the ir-responsive natural-phosphorescence, are more strongly affected by the direct effect from the Se-ions than that from the Cd-ions, both locating themselves substitutionally near the traps, and that the shallow traps are not so susceptible to an indirect effect caused by the elongation of atomic-spacing.

In conclusion, the author is grateful to Mr. K. Tōei and Mr. Y. Nakagawa of the Department of Chemistry for their useful advice in purification and analysis of the materials.

On the Infrared-Responsive Behaviors of (Zinc: Cadmium-Sulphide: Selenide)-Type Phosphor Families

V. Zinc: Cadmium-Sulphide: Selenide Phosphors

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(Received April 25, 1955)

Some (Zn : Cd)(S : Se) phosphors activated with Pb, Mn, Cu, Bi and Ag have been prepared. Their spectral infrared-responsivity and the decay of their natural and infrared-stimulated or -quenched phosphorescence as well as their luminescence and crystal structure are investigated. The results obtained show that the infrared-responsive behaviors of the (Zn : Cd)(S : Se) phosphors are qualitatively similar to those of the Zn(S : Se) and (Zn : Cd)S phosphors, which are reported in the previous papers, and that the infrared-responsive mechanism of ZnS phosphors are not substantially altered by the addition of CdSe.

1. Introduction

The optical properties of some (Zn:Cd)(S:Se) phosphors have been reported by several investigators[1]. The author prepared some (Zn:Cd)(S:Se) phosphors activated with various metallic elements and crystallized at two different temperatures. Their luminescence and spectral infrared- (abbreviated as ir-) responsivity as well as the decay-curves of their natural and ir-stimulated or -quenched phosphorescences were investigated by using the same apparatus as stated in the previous papers.

2. Preparation of Materials

Pure CdSe powder was prepared by the following procedures. In order to obtain about one third mole lot of pure CdSe, 300 g of $Na_2SO_3 10H_2O$ purified by repeated fractional-recrystallizations is dissolved in 2 l of distilled water. Into this Na_2SO_3 solution 30 g of purified Se[2] can be dissolved, forming a molecular compound $(Na_2SO_3)_2Se$. This solution is filtrated. (Solution A) Further, 100 g of purified $CdSO_4 8/3H_2O$[3] is dissolved in 2 l of distilled water. (Solution B)

1) H. W. Leverentz et al: *Preparation and Characteristics of Luminescent Materials* (John-Wiley & Sons Co. N.Y. 1948).

2) S. Asano: Jour. Appl. Phys. Japan **23** (1954) 527.

3) S. Asano: Science of Light **4** (1955) 16.

A small amount of the solution B is mixed with the total of the solution A at a room temperature, the mixed solution remaining still clear. When it is heated to boiling in a porcelain casserole on a sand-bath, dark-red precipitates are formed. The boiling is continued for about an hour under incessant stirring until the initial precipitate turns to redish-brown CdSe by the following hydrolytic reaction[4].

$$(Na_2SO_3)_2Se + CdSO_4 + H_2O \rightarrow CdSe\downarrow + H_2SO_3 + 2Na_2SO_4 \quad (1)$$

The supernatant solution is carefully decanted by discarding CdSe (plus occluded low solubility selenides). These procedures are repeated twice.

Especially in the case when traces of impurity-ions Cu^{2+}, Co^{2+}, Fe^{2+} and Mn^{2+} are in the solution A, these ions accelerate the oxidation of Na_2SO_3 to Na_2SO_4 by catalytic effect[6] and at the same time promote the reduction of neutral Se in $(Na_2SO_3)_2Se$ to Se^{2-} by the following reaction similar to (1)

$$(SO_3)_2Se^{4-} + H_2O \rightarrow Se^{2-} + SO_4^{2-} + H_2SO_3 \quad (2)$$

Since the solubility of selenides of heavy metals is as considerably low as that of their sulphides, colloid-like aggregation of the selenide-molecules of heavy metals will immediately occur. They may favorably become nuclei in the precipitation of CdSe. Hence, the ions of heavy metals in the solution A will be effectively carried away with discarded CdSe by the above co-precipitation procedure*.

400 cc of the solution B is then mixed with the decanted solution A and the similar procedure is repeated. The obtained pure CdSe is separated by a glass-filter.

In this procedure it is essentially important to establish a definite paucity of Cd^{2+} for the amount of $(SO_3)_2Se^{4-}$ in the mixed solution and to effect the hydrolytic reaction (1) at a carefully controled elevated temperature[6]. In the present case the ratio of mole concentration of Cd^{2+} to that of $(SO_3)_2Se^{4-}$ in the mixed solution was about 20%. A chemical analysis[7] of the substance produced

4) H. W. Leverentz: *Introduction to Luminescence of Solids.* (John Wiley & Sons Co. N.Y. 1950) p 476.

5) J. Milbauer et al: Chem. Listy. **15** (1921) 34.
F. Ishikawa: Riken-Iho (Tokyo, Japan) **3** (1924) 387.
S. Glasstone: *Text-book of Physical Chemistry* (D. Van Nostrand Co. N.Y. 1940) p 1104. Jour. Chem. Education **25** (1948) 278.

* This co-precipitation method may be effectively available also for the preparation of pure ZnSe powder. (cf. reference 2)

6) N. E. Gordon et al: U.S. Pat. 2, 176, 495 (1939).

7) W. W. Scott: *Standard Methods of Chemical Analyses.* (D. Van Nostrand Co. N.Y. 1939) Vol. 1. pp 201, 784.

under this concentration-ratio showed that it was a substantially stoichiometric compound of Cd and Se.

From the above filtrate pure CdSe may be obtained additionally through successive fractional-precipitations in a similar manner, if distilled water is supplied to the filtrate to compensate the evaporation loss before each mixing and 400×0.8^n cc of the solution B is added into the n-th filtrate to maintain the concentration-ratio at the rated value. By ten successive precipitations about 90% of the dissolved Se may be recovered as pure CdSe. Although the pH of the filtrate tends to become somewhat lower by repeating the precipitations as seen in the reaction (1), any symptom showing the dissociation of $(Na_2SO_3)_2Se$ and the co-precipitation of free Se with CdSe was not noticed.

The obtained pure CdSe precipitate is collected in one vessel and washed by decantation several times with hot distilled water, twice with pure conc. NH_4OH (to remove other cadmium compounds which may be produced by side reactions), and finally about twenty times more with hot distilled water. Pure CdSe is finally obtained as brown, homogeneous powder by evaporating to complete dryness in an electric drier at 110°C. The obtained CdSe powder is sealed in evacuated glass-ampoules and kept in darkness to protect against oxidation and photolysis[8].

Spectroscopic analysis (by Schimadzu QF-60) of the CdSe powder showed no detectable traces of foreign impurity-metals. The amount of Cu-impurity, if any, in it was estimated by the following procedures.

To each of 25 g lots of the CdSe powder was added 0.025, 0.25, 2.5, 5.0, 10.0 and 15.0 μg of pure Cu ($CuCl_2 2H_2O$ purified by triple-recrystallization) respectively. Then the Cu-activated and pure CdSe phosphors were prepared at 850°C in N_2-atmosphere. These phosphors had nearly black refrection-color under day-light and were non-luminescent*. Each 20 g of them was dissolved in pure conc. HNO_3 contained in a porcelain basin on a sand-bath and slow evaporation was continued until the deposited solids appeared dried. These solids were completely dissolved again in 300 cc of distilled water and SeO_2 in the solution was removed as completely as possible by passing a slow stream of SO_2-gas for a long time. The remaining solution obtained from each one of phosphor was treated with the extraction method similar to the case of CdS[9]. The obtained results showed that the Cu-amount in the CdSe powder may be estimated to be less than 10^{-5}%, which cannot affect the optical properties of the furnished phosphors.

* cf. the foot-note of the reference 3.

8) J. W. Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans-Green Co. N.Y. 1930) Vol. 10. p 779.

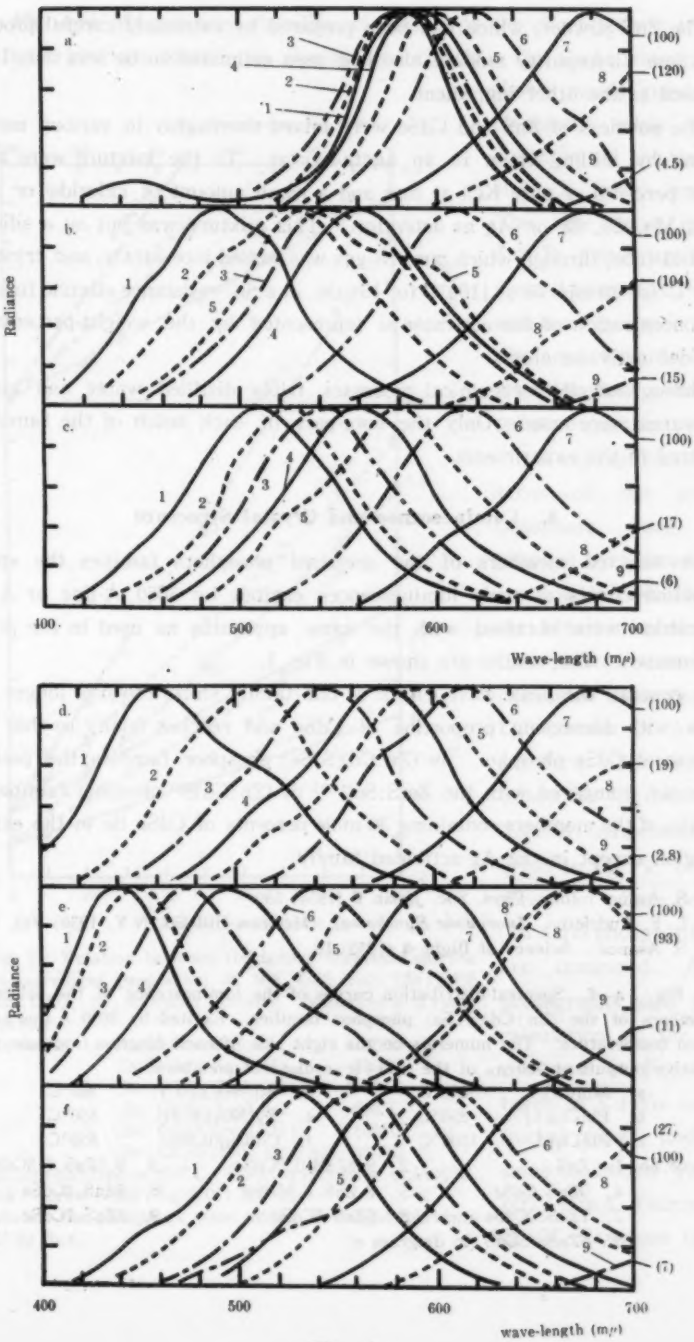

a.
b.
c.
d.
e.
f.
(100)
(120)
(4.5)
(104)
(15)
(17)
(6)
(19)
(2.8)
(93)
(11)
(27)
(7)
Radiance
400
500
600
700
Wave-length (mμ)

Fig. 1.

The ZnS powder, which had been prepared by extremely careful procedures and whose Cu-impurity amount also had been estimated to be less than 10^{-5}%[9], was used as the other ingredient.

The powders of ZnS and CdSe were mixed thoroughly in various mole proportions by milling them in an agate-mortar. To the mixture were added 2 weight percents of pure KCl as flux and a small amount of chloride or nitrate of Pb, Mn, Cu, Bi or Ag as activator. This mixture was put on a silica-boat in a silica-tube, through which pure N_2-gas was passed incessantly, and crystallized at 850°C for 20 min. or at 1100°C for 15 min. in a SiC-resistance electric furnace[10]. The concentration of the activator is represented by the weight-percentage of the added activator-atoms.

Throughout all the chemical processes, triply distilled water and insoluble glass-wares were used. Only the core-part of each batch of the sample was submitted to the experiments.

3. Luminescence and Crystal Structure

For selected members of the prepared phosphors families the spectral-distribution curves of their luminescences excited by 3650 Å-line at a room temperature were obtained with the same apparatus as used in the previous experiments[9]. The results are shown in Fig. 1.

In general, the peak wave-length of one family shifts towards longer wave-lengths with increasing proportion of CdSe and reaches finally to that of the ir-radiescent CdSe phosphor. In (Zn:Cd)(S:Se) phosphor families the peak-shift is so rapid, compared with the Zn(S:Se)[2)11)] or (Zn:Cd)S[3)] phosphor families, that the peaks of the members containing 30 mole percents of CdSe lie in the extreme-red region except in the Ag-activated family.

9) S. Asano: Jour. Phys. Soc. Japan **9** (1954) 580.
10) L. F. Audrieth: *Inorganic Syntheses*. (McGraw-Hill Co. N.Y. 1950) Vol. 3. p 17.
11) S. Asance: Science of Light **4** (1955) 16.

Fig. 1 a—f. Spectral-distribution curves of the luminescence of the selected members of the (Zn:Cd)(S:Se) phosphor families. Excited by 3650 Å-line at a room temperature. The numerals on the right side of each diagram indicate the relative outputs at 700 mμ of the (red+ir)-radiescent members.

a.	$Mn[Cl_2](1)$	850°C	d.	$Bi[(NO_3)_3](0.1)$	850°C
b.	$Pb[Cl_2](1)$	850°C	e.	$Ag[NO_3](0.01)$	850°C
c.	$Pb[Cl_2](1)$	1100°C	f.	$Cu[Cl_2](0.005)$	850°C

Curve no. 1. ZnS 2. 9.8ZnS.0.2CdSe 3. 9.5ZnS.0.5CdSe
4. 9ZnS.CdSe 5. 8.ZnS.1.5CdSe 6. 8ZnS.2CdSe
7. 7ZnS.3CdSe 8. 5ZnS.5CdSe 9. 3ZnS.7CdSe
8′. 5ZnSe.5CdS (in diagram e)

In Pb- and Mn-activated families of this type the characteristic features stated in the previous paper[3] can also be seen clearly. The Cu-activated family shows nearly regular displacement, while in the Ag-activated one the peak-shift is fairly irregular. The blue band in cub-ZnS:Bi disappears beyond a small proportion of CdSe. and then its green band is displaced towards longer wave-lengths with comparative regularity.

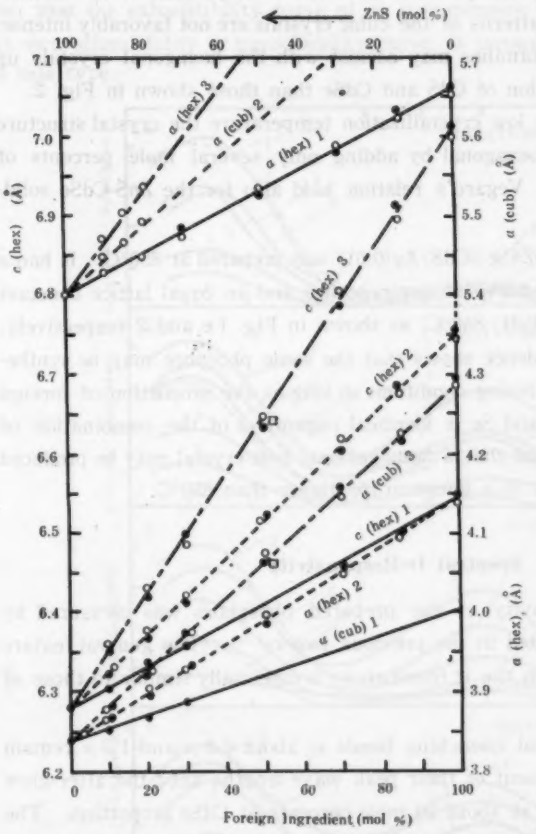


Fig. 2. Relation between the lattice constants and the foreign-ingredient proportion in the Zn(S : Se), (Zn : Cd)S and (Zn : Cd)(S : Se) phosphor families. Measured at a room temperature.

Curve no.		
1.	Zn(S : Se) : Bi(0.1)	1100°C
	Zn(S : Se) : Ag(0.01)	850°C
2.	(Zn : Cd)S : Cu)0.005)	1100°C
	(Zn : Cd)S : Ag(0.01)	850°C
3.	(Zn : Cd)(S : Se) : Pb(1)	1100°C
	(Zn : Cd)(S : Se) : Ag(0.01)	850°C

Circles : crystallized at 850°C. Dots : crystallized at 1100°C. Squares : 5ZnSe.5CdS : Ag(0.01) 850°C.

Into all the phosphors were added 2 weight percents of KCl as flux.

X-ray diffraction patterns of the prepared phosphors were photographed by Shimadzu Diffraction Unit DX-60. From the obtained photographs their lattice constants were calculated using pure cub-ZnS powder (a=5.40Å) as standard. The results obtained for the two crystallization temperatures are given in Fig. 2, on which those of Zn(S:Se) and (Zn:Cd)S phosphor families are compared. All the photographs used for the calculation of the lattice constants in Fig. 2 were taken by Cu-$K\alpha$ radiation (nickel filter) under the same conditions (Tube current: 14mA. Tube voltage: 30 kV. Exposure time: 30

min.). In the (Zn:Cd)S and (Zn:Cd)(S:Se) families crystallized at 850°C, the existence of cubic crystals mixed with hexagonal crystals was evidenced on the obtained roentogenograms by the patterns (200) and (400) peculiar to the former. Since these characteristic patterns of the cubic crystals are not favorably intense, the cubic crystals in these families may coexist with the hexagonal crystals up to somewhat higher proportion of CdS and CdSe than those shown in Fig. 2.

Even in the case of the low crystallization temperature the crystal structure tends to be predominantly hexagonal by adding only several mole percents of CdSe. As seen in Fig. 2, Vegard's relation hold also for the ZnS-CdSe solid-solution system.

Further, the phosphor 5ZnSe.5CdS:Ag(0.01) was prepared at 850°C. It had a similar spectral-distribution curve of luminescence and an equal lattice constant to those of 5ZnS.5CdSe:Ag(0.01) 850°C, as shown in Fig. 1 e and 2 respectively. The above experimental evidence shows that the same phosphor may be synthesized under the same crystallizing conditions so long as the proportion of foreign ingredient-atoms Zn, Cd, S and Se is identical regardless of the combination of the molecular ingredients, and that a homogeneous host-crystal may be produced by thermal diffusion at least at a temperature higher than 850°C.

4. Spectral Ir-Responsivity

The spectral ir-responsivity of the prepared phosphors was measured by means of the procedures stated in the previous papers[9)11)]. The general feature of the influence of CdSe upon the ir responsivity is essentially similar to those of ZnSe and CdS.

Both the stimulation and quenching bands at about 0.8 μ and 1.3 μ remain distinct showing no displacement of their peak wave-lengths until the after-glow loses its persistence visually at about 20 mole percents of CdSe proportion. The color of the stimulated phosphorescence (Pb: blue-green. Mn: orange) of one family is hardly affected by the addition of CdSe, while the color of its natural phosphorescence gradually changes with increasing proportion of CdSe.

Some of the obtained results are shown in Fig. 3. Pb- and Mn-activated families crystallized at 850°C show remarkable stimulation (cf. Fig. 3 a and b). while the Pb-activated one crystallized at 1100°C shows more quenching than stimulation which is weak. (Fig. 3 c) Ag-, Cu- and Bi-activated families show conspicuous quenching. Fig. 3 d shows one of the quenchability-characteristics typical to these three families. Besides, in Ag-, Cu- and Bi-activated families, weak stimulation is observed instantaneously at the beginning of irradiation,

especially on the members containing several mole percents of CdSe. (cf. Fig. 6)

Some of the exhaustibility curves, which were obtained by the procedures stated in the previous paper[3], are shown also in Fig. 3 by dotted curves. The fact that the exhaustibility curve of an ir-responsive member well coincides with its own stimulability or quenchability curve, is recognized also on the phosphors of this type.

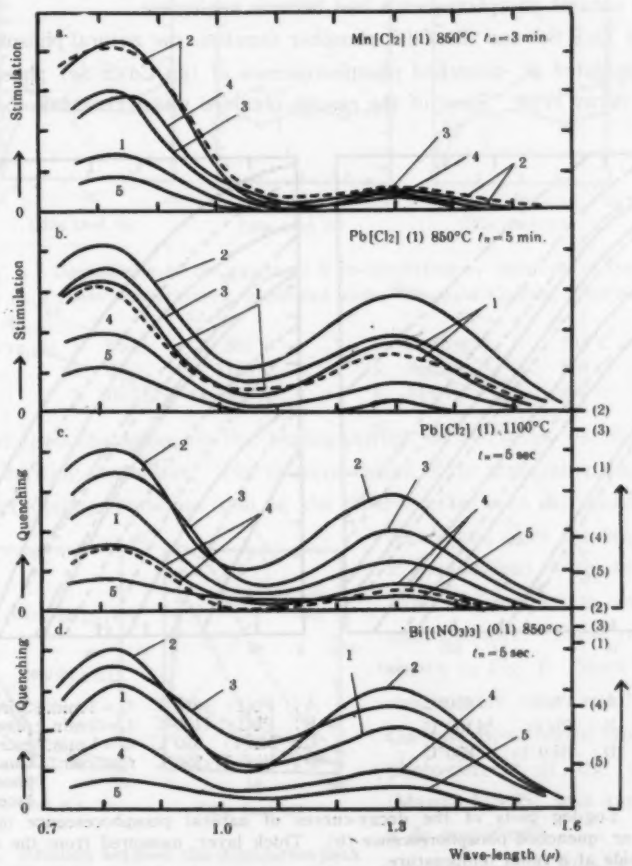
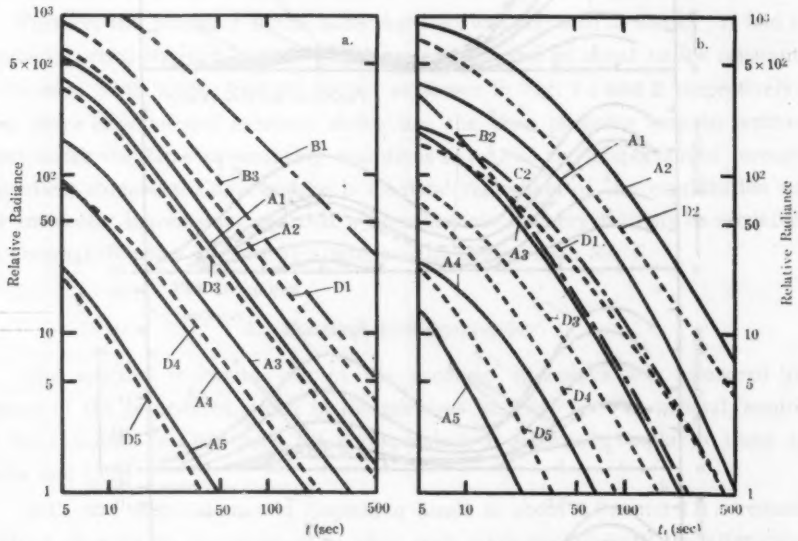


Fig. 3 a—d. Spectral ir-responsivity curves measured at a room temperature.
Curve no. 1. ZnS 2. 9.8ZnS.0.2CdSe 3. 9.5ZnS.0.5CdSe
4. 9ZnS.CdSe 5. 8.5ZnS.1.5CdSe
t_n: natural-decay duration before ir irradiation.
The ordinate of the lined mark on the right side of each quenchability diagram indicates the relative value of the natural phosphorescence light-sum of each member. Dotted curves show the exhaustibility curves of the corresponding members. (t_i=3 min.)

5. Decay of Phosphorescence

For all the ir-responsive members the decay-curves of natural phosphorescence and ir-stimulated or -quenched phosphorescence were measured by using the same apparatus as stated in the previous paper[3]. The decay-curves of ir-stimulated phosphorescence in Pb- and Mn-activated families were measured after the natural phosphorescence had become neglegible.

As in Zn(S:Se) and (Zn:Cd)S phosphor families, the natural phosphorescence and ir-stimulated or -quenched phosphorescence of (Zn:Cd)(S:Se) phosphors are of power-decay type. Some of the results obtained under the same exciting and



A: Pb(1) 850°C
B: Pb(1) 1100°C
D: Bi(0.1) 850°C

A: Pb(1) 850°C t_n=3 min. } Stimulated phosphorescence
B: Pb(1) 1100°C t_n=3 min. }
C: Mn(1) 850°C t_n=1 min. }
D: Bi(0.1) 850°C t_n=5 sec. Quenched phosphorescence

Fig. 4. Log-log plots of the decay-curves of natural phosphorescence (a) and ir-stimulated or -quenched phosphorescence (b). Thick layer, measured from the excited or irradiated side at a room temperature.

Curve no.	1	2	4	5
CdSe(mole %)	0	5	10	20

uv excitation: Mazda HL-300+Mazda UVD-2 Filter, distance at 30 cm for 3 min.
ir irradiation: Mazda Heating Lamp (100V. 250W. S-type)+Mazda IRD-1 Filter.
ir irradiance: 3.0 mW/cm²
t: time after the cessation of uv excitation.
t_n: natural-decay duration before ir irradiation.
t_t: time after the beginning of ir irradiation.

irradiating conditions are shown in Fig. 4, plotted on log-log diagrams. As an exception, the natural phosphorescence of Mn-activated members has a rapidly decaying exponential-part prior to a fairly persisteut power-decay tail-part. The values of the exponent n in the natural-decays are shown in Fig. 5, which were

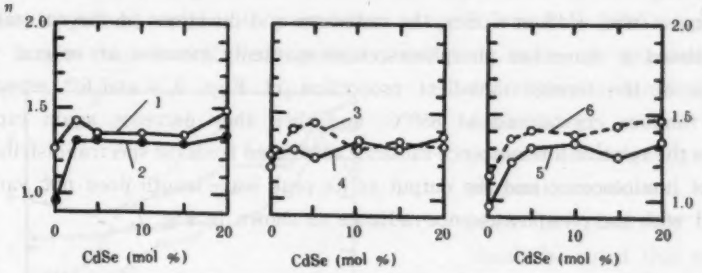


Fig. 5. Dependence of the exponent n in natural-decay upon the CdSe proportion at a room temperature. Measured ander the same exciting conditions as in Fig. 4.

Curve no.	1.	Pb(1)	850°C	4. Cu(0.005)	850°C
	2.	Pb(1)	1100°C	5. Ag(0.01)	850°C
	3.	Bi(0.1)	850°C	6. Mn(1)	850°C

determined from the slopes on the log-log-plotted decay-curves obtained under the same exciting conditions. The relative values of the stimulation peaks under the same irradiating conditions (that is, the difference between the photo-currents before and after the beginning of ir irradiation) were determined from the oscillogram obtained on each member. These resuits are shown in Fig. 6. Since the peak values were very small in Ag-, Cu- and Bi-activated families, the photo-current of the multiplier (Mazda MS-9S) was amplified by a dc amplifier[3].

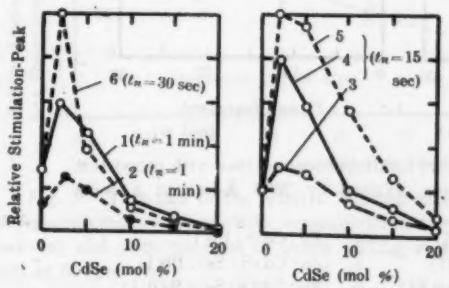


Fig. 6. Relation between the stimulation-peak and the CdSe proportion at a room temperature. Measured under the same exciting and irradiating conditions as in Fig. 4. Curve numbers refer to phosphor families as in Fig. 5.

As seen in Figs. 4 to 6, the items (1) to (5) on the decay characteristics of Zn(S:Se) and (Zn:Cd)S phosphor families stated in the previous paper[3], are also valid for the phosphors of this type without any modification. The time required to reach the straight part of the ir-

stimulated or -quenched decay-curve on a log-log plot is much longer in the phosphors crystallized at 850°C than in those crystallized at 1100°C, as shown in Fig. 4 b. This general tendency can be observed also in Zn(S:Se) and (Zn:Cd)S phosphors. (cf. Fig. 5 b in reference 3)

Starting from a ZnS phosphor and adding increasing proportion of foreign ingredient (ZnSe, CdS or CdSe), the radiances and durations of the natural and ir-stimulated or -quenched phosphorescences markedly increase at several mole percents of the foreign-ingredient proportion (cf. Figs. 3, 4 and 6)*, especially in the families crystallized at 850°C, and then they decrease again rapidly, whereas the relative luminescence-radiance calculated from the spectral-distribution curve of luminescence and the output at its peak wave-length does not vary in paralled with the phosphorescence-radiance as shown in Fig. 7.

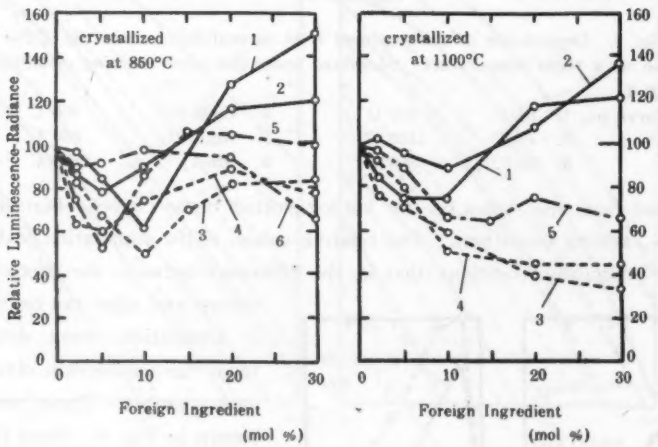


Fig. 7. Variation in the relative luminescence-radiance with proportion of foreign ingredient. Thick layer, excited by 3650 Å-line at a room temperature.

Curve no. 1. Zn(S:Se):Pb(1)
2. Zn(S:Se):Mn(1)
3. (Zn:Cd)S:Ag(0.01)
4. (Zn:Cd)S:Pb(1)
5. (Zn:Cd)(S:Se):Pb(1)
6. (Zn:Cd)(S:Se):Bi(0.1)

Referring to the experimental results obtained on all the prepared Zn(S:Se), (Zn:Cd)S and (Zn:Cd)(S:Se) phosphor families, the influence of these foreign ingredients upon the luminescence-radiance (luminescence-efficiency) of cub- and hex-ZnS phosphors under a given excitation by 3650 Å-line may be summarized as follows:

* cf. also Figs. 3, 5 and 6 in reference 3.

The relative luminescence-radiance of a hex-ZnS phosphor decreases nearly steadily with increasing proportion of CdS or CdSe, whereas that of a cub-ZnS phosphor decreases initially, rises a little then decreases again by the addition of CdS or CdSe.

When ZnSe is mixed into a cub- or hex-ZnS phosphor, its relative luminescence-radiance, in general, reaches to a maximum at an intermediate ZnSe proportion (fairly larger than several mole percents) and then decreases gradually. A definite rise in luminescence-radiance at several mole percents of foreign-ingredient proportion could not, in any case, be observed. Here should be noted that all the foregoing experimental data on luminescence- and phosphorescence-radiances are for phosphors which had not been subjected to deleterious chemical and mechanical (grinding) treatment after crystallization.

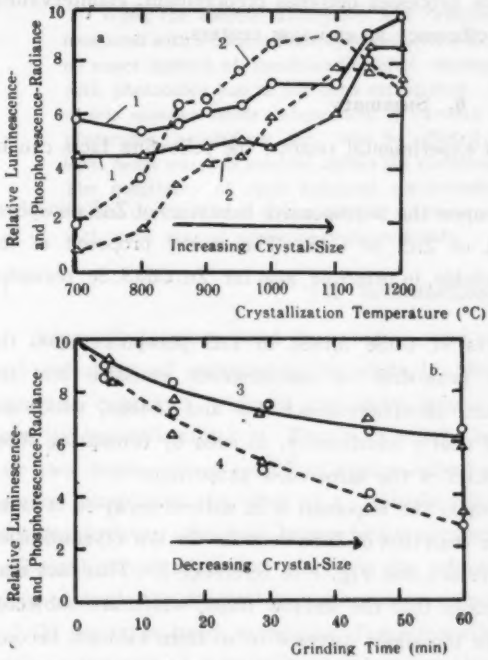


Fig. 8. Variation in the relative luminescence- and phosphorescence-radiances with crystallization temperature (a) and with the time of gentle milling in a ball-mill at 60 rpm. (b)

Curve no. 1. 9.5ZnS.0.5CdSe : $Pb[SO_4](1)$
2. 9ZnS.ZnSe : $Bi[(NO_3)_3](0.1)$
3. 9.5ZnS.0.5CdSe : $Mn[Cl_2](1)$ 850°C
4. 9ZnS.CdS : $Ag[NO_3](0.01)$ 1100°C

Circles: Relative luminescence-radiance unde constant excitation by 3650 Å.

Triangles: Relative phosphorescence-radiance 5 sec after constant excitation by 3650 Å.

Into all the phosphors 2 weight % of KCl was added as flux.

On the other hand, some phosphors were prepared having an identical host-crystal composition and various mean crystal-sizes by crystallizing identical ingredient-mixtures at various temperatures or by grinding a furnished phosphor in a ball-mill for various durations. Their relative luminescence- and phosphorescence-radiances were then measured under the same conditions[11]. These results are shown in Fig. 8. Since the mean crystal-size of a

phosphor has a nearly equal influence upon the luminescence- and phosphorescence-radiances according to the experimental results shown in Fig. 8, the anormalous increase in phosphorescence-radiance would not be explaind merely by assuming that the crystal-growth is promoted at several mole percents of foreign-ingredient proportion. As one of reasonable inferences, it may be mentioned that the trap formation would be fairly promoted by the addition of such a small proportion of foreign ingredient and that the effect of increasing number of trapped electrons contributing to phosphorescence processes becomes predominant, countervailing the reduction in light-emission efficiency at emission centers.

6. Summary

Surveying on the obtained experimental results, the following facts can be pointed out:

(1) The influence of CdSe upon the ir-responsive behaviors of ZnS phosphors is qualitatively similar to that of ZnS or CdS. The model proposed in the previous paper[11], therefore, available, in principle, also for (Zn:Cd)(S:Se) phosphor families.

(2) Referring to the effects of CdSe mixed in ZnS phosphors upon the atomic-spacing elongation, the peak-shift in luminescence emission and the persistence of ir-responsive natural-phosphorescence, Cd- and Se-ions, which are located substitutionally, operate nearly additionally, as seen by comparing these effects with those of ZnSe and CdS of the same mole proportion.

(3) The influence of CdSe upon the exponent n in natural-decay is of same order as that of CdS and weaker than that of ZnSe even for the low crystallization temperature. (cf. Fig. 5 in this report and Fig. 7 in reference 3) This fact may be explained by taking into account that the shallow traps, which are subjected to the weaker effect (resulting in the slight increase in n) from Cd-ions, become predominantly effective in the tail-part of the natural-decay, compared with those which are subjected to the stronger effect (resulting in the conspicuous increase in n) from Se-ions, or by assuming that the shallow traps in cubic crystals are more susceptible to the substitution by foreign-ingredient atoms than those in hexagonal crystals, which are predominant in (Zn:Cd)S and (Zn:Cd)(S:Se) phosphor families even when they are crystallized at a temperature fairly lower than the transition point 1020°C of the crystal structure of ZnS phosphor.

In conclusion, the writer is indebted to Mr. K. Tōei and Mr. Y. Nakagawa of the Department of Chemistry for their helpful advice in purification and analysis of the materials.

Some Considerations of the Balanced Spectroradiometry

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(Received April 10, 1955)

While the spectral absorption and reflectance of any sample can be measured with a double beam spectrophotometer with considerable accuracy, no exact method of spectroradiometric measurement of emission spectra with phototubes has as yet been established. *The accurate spectroradiometric measurements independent of various characteristics inherent to phototubes, amplifiers, etc., can be effected by setting up a reference light beam which is neutral within the wavelength range to be investigated.* The possibility of such balanced spectroradiometer to be used in the visible region is here discussed and a few examples are presented together with some data of preliminary experiments.

§ 1. Introduction

Spectrophotometers have been widely used to measure spectral transmissions and reflections of samples to be studied. Most of the modern types of the apparatus consist of a closed loop servo system with improved reproducibility, linearity and reliability.[1),2)] That is, the light beam from a light source is split into two beams using optical or electro-optical means. One serves as a "reference beam" and the other as a "sample beam," spectral balance at a light receiver between the two beams being accomplished by the movement of a calibrated optical attenuator placed in the reference beam, from whose displacement or angle the spectral transmission or reflection can be obtained.

On the other hand, in the case of spectroradiometric measurement of emission sources, the reference beam method has never been brought into practical use.[3),4)] The ordinary method consists in calibrating the spectral sensitivity of the light receiver by reference to a standard light source. But, due to the appreciable errors that might arise from the variations of light receiver response such as that caused by the fluctuation of amplifier gain, spectral fatigue effect of a

1) A. C. Hardy: J. O. S. A. **28** (1938) 360.
2) J. U. White, M. D. Liston: J. O. S. A. **40** (1950) 29.
3) V. K. Zworykin: J. O. S. A. **29** (1939) 84.
4) M. Yamada, H. Mitsuhashi, K. Akaki: Jour. Illuminating Eng. Inst. **8** (1954) 367 (in Japanese).

phototube,[5] etc., the results of the measurement are likely to come out unreliable. The only conceivable way of avoiding such difficulties is after all to establish a method in which a standard reference beam[6] is used and brought into balance by means of a suitable attenuator with the beam emerging from the emission source studied.

§ 2. Balanced Type of Spectroradiometer

One of the "balanced" types of spectroradiometer is shown schematically in Fig. 1.[7] Rotation of a semi-circular sector mirror enables one to introduce the

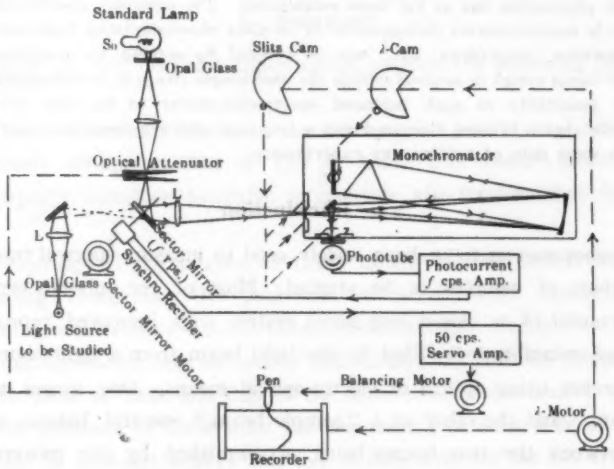

Fig. 1. Schematic diagram of the balanced spectroradiometer No. 1.

light beam emerging from a well-stabilized reference light source S_0 and that from a sample source S alternately into a monochromator. After being resolved into spectral components, the two beams are brought to focus onto a light receiver e.g. phototube or multiplier phototube, the output of which is amplified through an ac amplifier and demodulated by means of a synchronous rectifier operated by a sector mirror motor. As long as the intensities in the sample and reference beams are equal, the phototube receives constant light so that no ac output is gererated. If the intensity in the two beams becomes unequal, the

5) G. Kuwabara: Jour. Phys. Soc. Japan **8** (1953) 229.
6) F. J. Studer: J. O. S. A. **37** (1947) 288.
7) Unpublished. Nearly same type of a balanced spectroradiometer is being mounted by H. Takasaki, Faculty of Engineering, Tokyo University.

phototube will generate an ac signal the phase of which depends on which one of the beams is the stronger. This ac signal after being amplified will drive the servo-motor, and the optical attenuator will open or close until the intensities in the two beams become equal. Once a null condition is established, the spectral intensity of the sample beam E_λ relative to that of the reference beam $E_{0\lambda}$ can be deduced from the position of the linear optical attenuator. As the attenuation factor A of the optical attenuator can be assumed to be proportional to its linear displacement X, E_λ will then be related to $E_{0\lambda}$ by the equation

$$E_\lambda = E_{0\lambda} A \tag{1}$$

or

$$E_\lambda / E_{0\lambda} = A = kX \ (k = \text{const.}). \tag{2}$$

Thus if we want to obtain the spectral intensity distribution of the sample source itself, we should have an accurate knowledge as to the spectral intensity of the standard light source, which can be derived from its temperature provided the law of black body radiation can be assumed to hold. The most accurate method in spectroadiometry is to compare the sample beam directly with the emission from a black body furnace within which platinum is freezing, but provisions should then be made for maintaining the furnace temperature within a narrow limit in order to establish a well-defined reference source. This method is never fit for routine radiometric work. As is usual in photometry, a stabilized tungsten lamp with calibrated spectral distribution may conveniently be used as a substitute for the black body source.

It is evident that the above method is applicable only when the spectral intensity of the reference beam is stronger than that of the sample for all the wavelengths in question; in the opposite case some other device must be invented, as will be described later.

If it be required that the linear displacement of the optical attenuator should be proportional to the spectral intensity of the sample, the spectral intensity $E_{0\lambda}$ of the standard light source must be made constant, independent of wavelength. Since when

$$E_{0\lambda} = E_0 = \text{const.}, \tag{3}$$

it immediately follows from equation (2) that

$$X = E_\lambda / kE_{0\lambda} = KE_\lambda \tag{4}$$

where

$$K = 1/kE_{0\lambda} = 1/kE_0 = \text{const.} \tag{5}$$

Inasmuch as such a "neutral standard light source" as will satisfy the condition (3) cannot be available by itself, some automatic contrivance must be used

which allows a conventional light source to be transformed into a neutral source with stabilized brightness. One of the means to produce the secondary neutral beam is illustrated in Fig. 2. The light beam from a tungsten lamp S, after

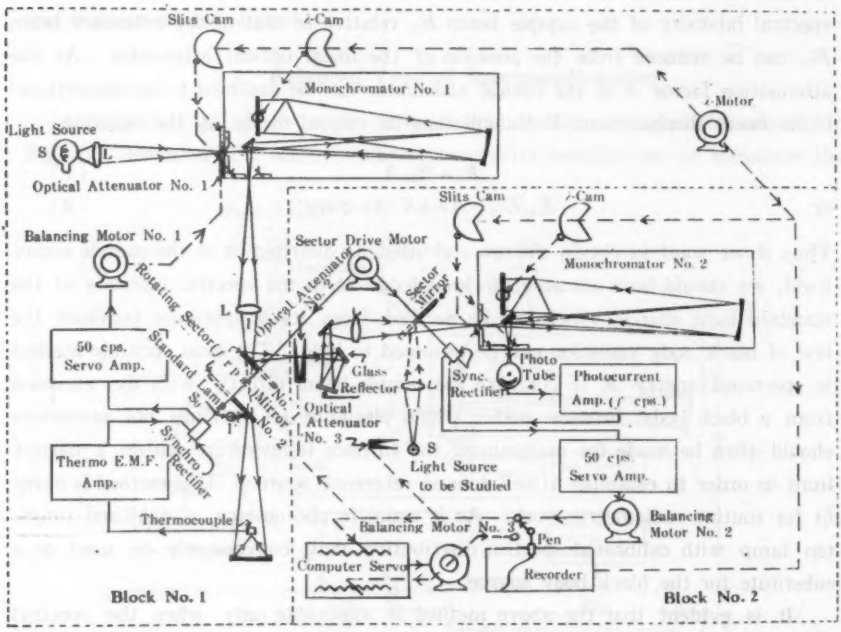

Fig. 2. Schematic diagram of the spectroradiometer No. 2.

being resolved into monochromatic components by means of a monochromator, No. 1, is divided into two beams by a rotating semi-circular mirror No. 1. One is fed to a radiation thermocouple coupled with a device which, as described in the next paragraph, is capable of neutralizing the intensity of the output beam of the monochromator in the whole wavelength region to be measured. The other beam consisting of the monochromatic beam thus neutralized can be used as a reference beam.

The neutralizing device is as follows: The chopped monochromatic beam I is brought to focus on the thermocouple alternately with a white beam I′ from another light source S_0 of considerably small power whose brightness can be well-stabilized for a sufficiently long time by virtue of its small wattage. Any difference in intensity between these two beams induces ac thermoelectromotive force which after being amplified operates a servo amplifier and controls the

monochromator input light intensity by adjusting the optical attenuator No. 1 placed in front of the entrance slit of the monochromator until the difference becomes zero. Thus we may obtain the light source with constant spectral intensity independent of wavelength. In recent years thermocouples of high speed response have come into frequent use as a radiation detector in infrared spectrophotometers and ***inter alia*** the electronic techniques of amplifying very small thermoelectric voltage have been remarkably improved, so that the above method is quite feasible even by the use of a tungsten lamp S with medium intensity in the visible region.

The basic principle of the designs can readily be seen from the figure. The balanced spectroradiometer is composed mainly of two parts, block No. 1 and block No. 2, the former being a constant energy "monochromator" and the latter a spectrometer of the balanced type. The two radiation beams I and I," the former emerging from the monochromator No. 1 and the latter from the emission source to be studied, are alternately introduced into the monochromator No. 2 and then fed to a multiplier phototube situated behind the exit slit. The method of comparing the two beam intensities I and I" is entirely the same as employed in the aforementioned balanced spectroradiometer shown in Fig. 1. The position of the attenuator No. 2 which is a measure of the spectral intensity of the sample, is traced on a pen recorder for the wavelength range where the spectral intensity of the reference source E_0 is stronger than that of the sample source E_λ. The curve obtained will then give none other than the spectral distribution of the sample source.

It likely happens that the spectral intensity of the reference beam E_0 is smaller than that of the sample beam E_λ. Then it is so devised that the optical attenuator No. 3 situated close to the sample source will be actuated to make equal the intensities of the two beams. The function of the attenuator No. 3, however, is not in every respect the same as that of the attenuator No. 2, since in this case its displacement is not proportional to the spectral intensity of the sample E_λ but is equal to the ratio of E_λ to E_0. If one wishes to make the recorded curve directly indicate the spectral intensity distribution E_λ and further to establish a smooth connection of the curve with that obtained within the range where E_0 is larger than E_λ, one is compelled to have recourse to a mechanical or an electrical computer or a cam mechanism between the attenuator No. 3 and the tracer or to the use of a non-linear optical attenuator. One of the electrical computers of a simple design is illustrated in Fig. 3. The output voltage of the photocurrent servo amplifier drives the optical attenuator No. 3 to compensate the difference in intensity by weakening the sample beam. For

securing the linearity of the record, the linear resistance R_R of a recorder potentiometer carried by the balancing motor No. 3 must be made to be inversely

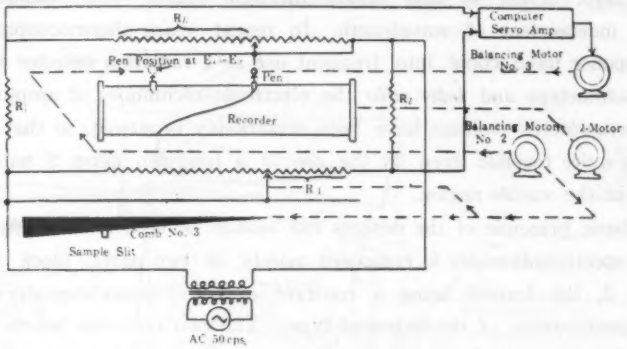

Fig. 3. Electrical computer network (illustrated for the case $E_\lambda=3E_0$)

proportional to the linear resistance R_A carried by the attenuator No. 3. Such manipulation can easily be performed with an electrical bridge network. Scanning process accompanying the displacement of the attenuator No. 2 continues until E_λ becomes equal to E_0, when by the action of a relay the pen carriage is disconnected from the motor No. 2 to be connected with the motor No. 3 and the computer comes into operation. The relation

$$R_R \cdot R_A = R_1 \cdot R_2 = \text{const.} \qquad (6)$$

which holds for the network in the balanced state is always satisfied while the resistance is changed automatically by the action of the recording motor No. 3 and the attenuator drive motor No. 2. In the example shown in the diagram, maximum spectral intensity of the sample source E_λ is limited to five times the reference intensity E_0. Maximum ratio in intensity of E_λ to E_0 increases with the attenuation factor and its gradient of the attenuator No. 3.

§ 3. Accuracy of the Balanced Spectroradiometer

Inasmuch as the major part of the above-mentioned spectroradiometer is included in a servo loop and the light receivers are designed to be sensitive only to the unbalance in intensity between two beams, the photometric errors arising from phototube fatigue,[5] time variation of spectral sensitivity of the photosurface, fluctuation of amplifier gain or distortion accompanying amplification, are completely eliminated. The sample source studied is outside the main closed loop, i.e. it is a "heterogeneous" light source. But this is inevitable when we

measure the emission spectra of the source quite different in nature from the reference source. If possible, however, it is preferable to excite the sample source with the same electric power supply as for the source S which is to be neutralized. Utmost care should be taken in designing the servomechanisms, because the apparatus contains two light receivers with different time constants; besides the error of such a closed system may depend on the gain in the amplifier as well as on the energy difference generated by the unit displacement of the attenuator. Steady as well as transient errors can, however, be reduced to a negligible amount by the use of well-designed servomechanisms. Accordingly the accuracy of the balanced spectroradiometer may be considered to be dependent mainly on the spectral neutrality of the reference beam and the linearity of the optical attenuator Nos. 2 and 3.

Gold black is one of the soots which are often used as radiation receivers of thermocouples for infrared spectrophotometry. To check its neutrality, spectral characteristics of a thin gold black layer deposited on a glass substratum in an atmosphere of nitrogen was measured with a spectrophotometer of Beckman type. In Fig. 4 are shown diffuse spectral reflectivity R and transmittance T in the visible region, the former being obtained by assuming a layer of Ba_2SO_4 as 100% reflector. A slight hump is seen in each distribution near the wavelength of 4800Å. A similar measurement has been reported by Harris et al with gold black surfaces on cellulose nitrate films.[8] With gold black we could not obtain such a neutral surface as will be expected of a perfect black body for the visible range. Receivers of better neutrality might be obtained with other material of adequate thickness at the expense of rapid time response.

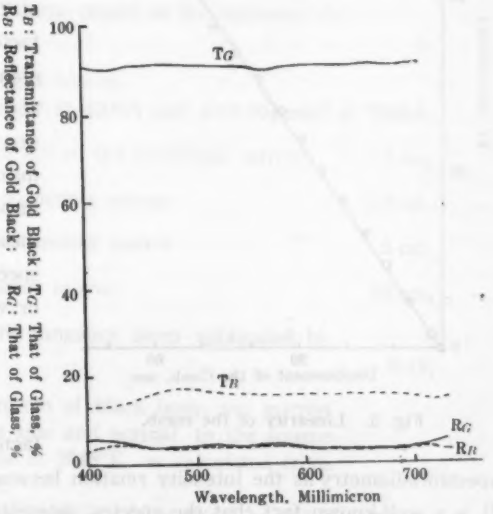

Fig. 4. Spectral characteristics of gold-black.

Absorbance A, measure of efficiency with which the impinging radiation is transformed into heat, is related to transmittance T

8) L. Harris et al: J. O. S. A. **38** (1948) 582.

and reflectance R by the equation

$$A=1-T-R\,. \qquad (7)$$

But the absorbance A of gold black cannot be determined exactly by the aid of (7) and the data given in Fig. 4, since the effects a glass backing and of a reference reflector on the measured data can hardly be taken into consideration quantatively. It is very probable, however, that the deviation from perfect neutrality lies within ±2 percent.

In addition to the neutrality test, we examined the optical linearity of a comb-type attenuator which was made of five blades of steel of moderate hardness and was 60 mm in length and 6 mm in width as its maximum. A photo-cell with a slit placed behind the comb received a parallel light beam which was incident on the comb from one side and transmitted through the gaps of the blades. Fig. 5 shows the output current obtained as the comb position i.e. attenuation factor was varied. The linearity is deteriorated at a few points. Maximum attenuation factor of 2: 100 is attainable with it. A factor as large as 5: 1000 may be obtained with an attenuator made of suitable material with more precision.[9] It is apparent that the maximum attenuation factor is an important factor for making accurate measurement of some emission spectrum having extremely strong or weak intensity.

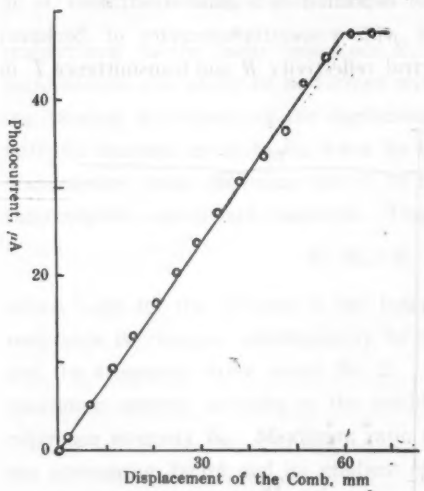

Fig. 5. Linearity of the comb.

§ 4. Discussions

One of the most important factors in the balanced type of spectroradiometry is the intensity relation between reference and sample beams. It is a well-known fact that the spectral intensity of radiation emitted from the visible light source with continuous spectrum is generally the faintest at the violet end as is the case with a tungsten lamp, and in addition the radiation detector with neutral sensitivity like a thermocouple has only very low sensitivity.

9) J. U. White, M. D. Liston: J. O. S. A. **40** (1950) 93.

For designing the monochromator No. 1, therefore, the available intensity of radiation in this region is to be evaluated by taking into account two conflicting factors: the resolving power of the monochromator and the sensitivity of the thermocouple. The available energy can be calculated as follows. Suppose that the spectrometer used in the quartz Beckman spectrophotometer of the type DU[10] plays the part of the monochromator No. 1 with the following conditions.

Color temperature of the tungsten lamp used as the light source S: 2848°K,

Spectral band width throughout the whole wavelength range: 20Å,

Opening width of the entrance and exit slits, both bilateral and ganged, their opening being varied with wavelength corresponding to the band width of 20Å:
0.17 mm at 4000Å and 0.021 mm at 7000Å[11]

Height of the slits: 15 mm,

Magnification of the light source image at the entrance slit by the condenser mirror: 5,

Effective aperture of the light source:
3×0.03 mm² at 4000Å and 3×0.004 mm² at 7000Å,

Distance from the entrance slit to the condenser mirror: 17 cm,

Effective diameter of the condenser mirror: 1.7 cm,

Effective diameter of the collimator mirror: 5 cm,

Focal length of the collimator mirror: 50 cm,

Effective solid angle of the tungsten lamp subtended by the condenser mirror: 0.19,

Energy radiated per square cm of black body, per micron wavelength band, to one side and normal to the source plane per unit solid angle at 2848°K, as calculated from the table by P. Moon[12]:
4.46 watt/cm². micron. solid angle at 4000Å and 53.1 watt/cm². micron. solid angle at 7000Å.

The radiation output of the monochromator can easily be calculated to be

10) H. H. Carry, A. O. Beckman: J. O. S. A. **31** (1941) 682.
11) H. M. Haendler: J. O. S. A. **38** (1948) 417.
12) P. Moon: J. O. S. A. **38** (1948) 291

3.5×10^{-6} watt 4000Å

and

5.41×10^{-6} watt at 7000Å.

On account of the optical absorption or reflection losses to be sustained on the way from the light source to the thermocouple, the available energy is further reduced to about one-tenth of the calculated values, that is,

3.5×10^{-7}watt at 4000Å and 5.4×10^{-7} watt at 7000Å.

The difference in intensity of the two beams from the sources S and S_0 of the order of 10^{-9} watt causes the attenuator No. 1 to produce a motion of one percent of its full length. On the other hand, the least detectable power of a thermocouple limited by Johnson noise is reported to be about 3×10^{-10}watt.[13),14)] Thus the radiation energy from the monochromator is tolerably sufficient to actuate the optical attenuator, but we cannot expect a completely satisfactory operation with fair signal-to-noise ratio. It is to be recommended to use a monochromator with larger aperture and dispersion in place of the one cited above in order to obtain better performance.

There is a large difference in sensitivity between the radiation thermocouple and the multiplier phototube which is used as a radiation detector of the output beam from the monochromator No. 2. The least detectable power of a multiplier phototube limited by the fluctuation noise that originates in the thermionic emission at the photocathode is about 10^{-15} watt.[15),16),17)] Accordingly the sample beam of which the intensity is considerably feeble as compared with the reference beam can be measured with the multiplier phototube; only it might possibly occur that by the use of a single attenuator the sensitive balancing between the reference and sample beams can hardly be attained. It will then be required to set up an additional attenuator in the reference beam behind the comb attenuator No. 2. A glass or quartz surface may be used for that purpose, since from Fresnel's reflection formula

$$r=\frac{1}{2}\left\{\frac{\tan^2(\varphi-\psi)}{\tan^2(\varphi+\psi)}+\frac{\sin^2(\varphi-\psi)}{\sin^2(\varphi+\psi)}\right\}, \qquad (8)$$

13) L. C. Roess: R. S. I. **16** (1954) 172.
14) H. Mitsuhashi: to be published.
15) R. W. Engstrom: J. O. S. A. **37** (1947) 420.
16) R. C. Jones: Advances in Electronics Vol. 5 (1953) 1.
17) S. Fujita: Science of Light **3** (1954) 25.

it can be foreseen that attenuation ratio less than 10^{-2} may be obtained with twice repeated reflections at optically polished surfaces of glass (see Fig. 2). (It is to be noted that the optical attenuator No. 1 may not necessarily be a comb, but for instance a photographic plate whose density varies continuously along its lateral direction by a factor of about ten.)

As the aforementioned balanced spectroradiometer is contained in a close servo-loop, ***the light receivers serve merely as detectors of difference in intensity between the double beams, so that their linearity and the fatigue effect never come into play. A high grade of reproducibility or stability of the amplifier is not needed.*** These characteristics are the eminent features of this type of spectroradiometer. Owing to the features as well as to the substantial improvements in the balancing arrangement that can be brought about by the circumspect optical design, we are now in a position to state that ***the balanced spectroradiometer nearly perfectly satisfies the " necessary condition for the spectral photometry of high accuracy."***[5]

§ 5. Final Remarks

Demands are being increased for making accurate measurements of relative intensities of continuous spectra for different wavelength range in the field of applied optics such as illumination engineering, colorimetry of the radiating light source and television optics. Therefore the methods of radiometric measurements should be reviewed anew from the different standpoints of modern instrumental techniques. The author has entered into details on these lines and succeeded in devising a method of constructing a balanced spectroradiometer which meets the requirements, although it may not be unique method ever conceivable.

§ 6. Acknowledgement

It is the author's pleasure to acknowledge his indebtedness to Dr. G. Kuwabara of Tokyo University for the remarks and discussions and to Dr. M. Okamatsu of Electrotechnical Laboratory and Dr. S. Fujita of Osaka University for their helpful discussions. The author wishes particularly to thank Mr. M. Nakamura of the Institute for Optical Research, Tokyo University of Education, for the preparation of gold black layers.

Raman spectra of some simple and complex halides of cadmium

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(Received, March 23, 1955)

Abstract

Raman spectre of aq. solutions of $CdCl_2$, KCl. $CdCl_2$, 2 KCl, $CdCl_2$, $CdBr_2$, KBr. $CdBr_2$, have been photographed with negative results. A solution of 2 KBr.$CdBr_2$, however, shows a Raman line, attributable to the $CdBr_4^{--}$ ion.

A solution of CdI_2 yields a Raman line the intensity of which increased, without change in frequency, on the addition 1 and 2 mols. of KI.CdI_2 (crys.) also shows a weak line with almost the same shift.

The results show that CdI_4^{--} ions exist not only in 2 KI.CdI_2 solution, but even in pur CdI_2 Crys and solution both. The various physico-chemical data for CdI_2 solution also point to the same conclusion.

1. Introduction

Halogen atoms in the divalent chlorides and bromides are known to have a layer structure. They are less polarizable than iodine atoms and are therefore typical of a less degree of distortion than prevails in the CdI_2 structure.

According to Ferrari and Giorgi, cobalt, ferrous and manganese bromides have crystal structure of the CdI_2 type while $CdBr_2$ exhibits a rhombohededric cell of the $MgCl_2$ type.

It is well known that under similar conditions CdI_2 ionizes less rapidly than $CdBr_2$ and the latter less readily than $CdCl_2$.

These facts go to show that a distinct difference should be expected in the structure of these three compounds.

Coming to the study of Raman effect, it is apparent that not only the results obtained for $CdCl_2$, $CdBr_2$, and CdI_2 and their complex compounds by different workers are conflicting but also the very chemistry of their behaviour in aq. solution is differently interpreted by them.

To take an example Venkateswaran[1], from a study of Raman effect of aq. solution of $CdBr_2$ and 2KBr.$CdBr_2$ concluded that the line obtained in each

1) Venkatenswaran, Proc. Ind. Acad. Sci., **1**, (1935) 850.

case was due to the oscillation of unionized $CdBr_2$ molecule, addition of KBr only effecting the degree of ionisation. He thus concluded that there was not sufficient evidence for the formation of complex ions of the type $CdBr_4^{--}$ either in $CdBr_2$ or in 2KBr. $CdBr_2$ solution.

Braune and Engelbrecht[2] failed to get any definite line in aq. sols. of cadmium halides but obtained intense lines in the sols. of mixtures of CdI_2 and $CdBr_2$ and the corresponding alkali halide which they attributed to CdI_4^{--} and $CdBr_4^{--}$ ions respectively.

Lastly, Delwaulle, Wiedeman and Franz[3] maintain that an aq. solution of both $CdBr_2$ and 2KBr.$CdBr_2$ contain ions of the type $CdBr_4^{--}$.

The present work was undertaken to throw some more light on the subject.

The experimental arrangement was the one usually adopted. Pure analytical substances were used.

2. Results

Substance	Exciting line	$\Delta\nu$	Intensity
$CdBr_2$ Crys.	—	no line	
$CdBr_2$ sol.	—	no line	
KBr. $CdBr_2$ (sol).	—	no line	
2KBr. $CdBr_2$.	λ 4358.34	166.5	s
	5461.73	168	s
CdI_2 Crys.	4358.34	118	w
CdI_2 sol.	4358.34	130	m
	5461.73	130.6	m
KI. CdI_2 (sol).	4358.34	131	s
	5461.73	131.7	s
2 KI. CdI_2 (sol).	4358.34	131.5	v. s.
	5461.73	132	v. s.

Discussion

Cadmium bromide (*Crystal and solution*).

Of the previous workers Krishnamurti, could observe no Raman line for crystalline $CdBr_2$ although according to Venkateswaran it shows a line at $\Delta\nu$ 153. The author could not succeed in getting any Raman line, pointing to the fact that cadmium bromide exists mostly in the ionic condition even in crystals.

Braune and Engelorecht failed to obtain any Raman line for $CdBr_2$ (sol.), although Vekateswaran did observe a line at $\Delta\nu$ 154 for a 50% sol. implying thereby as in the previous cases that cadmium bromide even in solution exists

2) Braune & Engelbrencht, Z. Phy. Chem. **19 B**, (1932) 303.
3) Delwaulle and others, 1939, Comp. Rend, **208**, (1939) 1818.

in the molocular condition.

Delwaulle and others reported for an aqueous sol. of $CdBr_2$ not less than four lines $\Delta\nu$ 53, 62, 166 and 186 and they attributed these to the ion $CdBr_4^{--}$ formed as a result of auto-complex formation thus:—

$$CdBr_2 \rightleftarrows Cd^{++}+2Br^-$$

$$Cd^{++}+2Br^-+CdBr_2 \rightleftarrows Cd\ [CdBr_4]$$

The fact that crystalline $CdBr_2$ showed no Raman effect led the author to anticipate that its aq. sol. would show still more negative results. But for comparison it was thought desirable to try an aq. solution also. An 11% solution was first tried but it yielded no line; next a 50% solution was used but it again failed to show any Raman line. On the strength of these results the authors conclusion is that cadmium bromide exists mostly in the ionized condition both in solid and in solution.

2KBr. $CdBr_2$ (sol.)

According to Venkateswaran, $CdBr_2$ and 2KBr. $CdBr_2$ give practically the same Raman shift with a difference in their intensity. Such an observation led him to conclude that even in 2KBr.$CdBr_2$ there are no $CdBr_4^{--}$ ions present and that the addition of 2KBr, results only in the strengthening of the line already there.

Although failing to obtain a line for $CdBr_2$ (sol.) Braune and Engelbrecht did obtain an intense line at 160 for 2KBr.$CdBr_2$ and they attributed it to the formation of complex ion $CdBr_4^{--}$ in the solution.

The French workers have reported four lines 53, 62, 166 and 181 for 2KBr. $CdBr_2$ as also for $CdBr_2$ solution, and they attributed these to the tetrahedral $CdBr_4^{--}$ ion supposed to be present in both the solutions.

While from the author's results, $CdBr_2$ does not show any Raman lines, solution of 2KBr.$CdBr_2$ does show a Raman line at 166 by excitation with both 4538.34 and 5461.73. The microphotograph shows no other component.

The presence of the Raman line in 2KBr.$CdBr_2$ (sol.) is indicative of the fact that the structure of this compound is entirely different for that of $CdBr_2$ alone. It seems probable that like $HgCl_4^{--}$ there may exist in the present case $CdBr_4^{--}$ ions which give rise to one of its characteristic frequencies—a view upheld by Braune and Engelbrecht also.

Cadmium Iodide.

A number of evidences like freezing point, depresion, conductivity and transport number[4] go to show that CdI_2 exists in a very much different state

4) Gmelins, Handbuch der anorg. chemie. (1925) No. 33.

from that of its analogies $CdCl_2$ and $CdBr_2$. CdI_2 in solution has been assumed to exist as a complex compound containing CdI_4^{--} ions.

CdI_2 (Crys. and solution).

Krishnamurti obtained for the crystal three week lines at 105, 345 and 395 while Venkateswaran reported only one at $\Delta\nu$ 113. Both attributed the lines to the molecule CdI_2. The author obtained a single line at $\Delta\nu$ 118 for the crystal.

For CdI_2 solution Venkateswaran observed a shift at $\Delta\nu$ 119 while Braune and Engelbrecht failed to obtain any line. Delwaulle and others[5] obtaided results similar to their results for $CdBr_2$ solution viz four lines at $\Delta\nu$ 36,44, 116 and 144 which were attributed to CdI_4^{--}.

The author succeeded in getting only one line for the solution at 130 which, it may be noted, is the mean of 116 and 114—the lines obtained by Delwaulle and others.

The Raman line obtained should be attributed either to the unionized CdI_2 molecule or to the CdI_4^{--} ion, formed as a result of auto-complex formation. Some of the previous workers have attributed it to the molecule CdI_2, but there are strong reasons against this viewpoint:—

1. Conc. CdI_2 (sol.) has been shown from physio-chemical data to consist of CdI_4^{--} ions.

2. The frequency shift given by the molecule CdI_2 should be higher than that of CdI_4^{--} ion. Actually it is found that the frequency shift shown by CdI_2 (Crys.) is smaller than that given by CdI_2 or $2KI.CdI_2$ solution and the latter must contain CdI_4 ions. Thus the line given by CdI_2 (Crys.) is also due to CdI_4^{--} ion.

3. Since HgI_2 is known to give 155, it is expected that the CdI_2 molecule should show a higher frequency shift in view of the lower atomic wt. of Cd. Actually the shift observed in an aq. solution of CdI_2 is lower than that for HgI_2 molecule. This means that CdI_2 (sol.) exists not as simple CdI_2 molecule but as a more complex ion.

4. Braune and Engelbrecht have compared the value of

$$\frac{\text{Heat of Dissociation}}{\text{Force constant.}}$$

for the various mercury halides as also for CdI_2. They found an abnormal value for CdI_2 solution which can only be explained on the assumption of some such mechanism as auto-complex formation.

5) Delwaulle and others Compt Rend. **206**, (1938) 187.

KI. CdI_2 and 2 KI.CdI_2 (Solution).

A solution of KI.CdI_2 for which no previous data are available, was found to give essentially the same line as in CdI_2(sol.) viz. $\Delta\nu$ 131. The intensity is, however, slightly greater than in the previous case. This unequivocally shows that the line is due to CdI_4^{--} ions and that the increase in intensity is due to the increase in the number of CdI_4^{--} ions.

No evidence is available for the formation of CdI_3^- ion.

Venkateswaran reported for 2KI·CdI_2 solution only one line at $\Delta\nu$ 119 which is the same as that observed by him in CdI_2 solution. The fact that the shift is the same in both led him to conclude, as in the case of $CdBr_2$ that "the Raman effect date of the solutions of cadmium halides do not offer any evidence for the formation of complex ions in them." Braune and Engelbrecht obtained a line at $\Delta\nu$ 118 which they attributed to CdI_4^{--} ion.

The French workers obtained the same four lines as in CdI_2 solution viz $\Delta\nu$ 36, 44, 116 and 144 and attributed them to CdI_4^{--} ion.

The author has obtained oniy one line at $\Delta\nu$ 132 which being the same as before, may be attributed to CdI_4^{--} ion. The intensity of the line has still further increased, which is not unexpected.

In a solution of 2KI.CdI_2, remembering that I atom is easily polarizable, there must be present CdI_4^{--} ions, which give rise to $\Delta\nu$ 132; since the same line is shown by pure CdI_2 solution it may be concluded that CdI_4^{--} ions are present in CdI_2 solution also. The formation of such a complex ion could take place as shown

$$2CdI_2 \rightleftarrows Cd(CdI_4)$$

This means that half the number of Cd ions have gone over to the acid radical. This should result in the development of abnormal physico-chemical properties in CdI_2 solution.

The constitution of CdI_2 has been the subject of interesting discussion. If two workers agree on the results they disagree on the interpretation and vice versa.

Whereas Venkateswaran maintains that no evidence is found for the existence of any complex ion such as CdI_4^{--} even in 2KI.CdI_2 (much less in CdI_2) solution, Braune and Engelbrecht are of the opinion that the line obtained with 2KI. CdI_2 solution is due to the CdI_4^{--} ion. Delwaulle and others obtained four lines (which is the number theoretically required assuming the tetrahedral structure of CdI_4^{--} ion) not only in 2KI·CdI_2 solution but also in aq. CdI_2 alone.

The author obtained a single line. The line, not only in 2KI.CdI_2 solution

but also in CdI_2 solution alone, must be attributed to the complex CdI_4^{--} ion and in support of this conclusion several evidences have been adduced.

The author desires to express his grateful thanks to Dr. P. N. Sharma and to late Mr. M. R. Nayar for their kind interest and guidance in the present work.

Raman spectra of Iodic Acid at different dilutions

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(Received, March 23, 1955)

Abstract

Physico-chemical properties of aq. solutions of iodic acid have shown breaks in the curves at 0.09N and 0.44N, which have been interpreted as transition points in the depolymerisation of (HIO_3) molecules.

To obtain Raman spectral evidence on this problem, solutions were prepared for concentrations ranging on either side of the transition points viz. 0.03N, 0.07N, 0.2N and 1N and also of a more concentrated solution 4.5N.

The concentrated solution gives three bands, of which the most intense and broadest one consists of three components at $\Delta\nu$ 789, 806 and 826 in the order of decreasing intensity. The second strongest band consists of three components at $\Delta\nu$ 317, 332 and 354, while the third band consists of two components at $\Delta\nu$ 642 and 653.

A 1N solution gives essentially the same spectrum as the more concentrated one.

A 0.2N and 0.07N solutions each gives only one line at about $\Delta\nu$ 805 which consists of two components at $\Delta\nu$ 804 and 824 in the case of 0.2N, and of three components $\Delta\nu$ 804, 812 and 828 in the case of 0.07N.

A 0.03N solution of the acid gives a line (single) at $\Delta\nu$ 811 and with a 0.2N KIO_3 solution the same frequency shift is obtained, suggesting thereby that the former frequency is due to IO_3^- ion. Other lines have been interpreted on the theory of polymerisation or coordination.

1. Introduction

The constitution of iodic acid and its salts has been the subject of investigation in recent years by a number of workers from different points of view. The crystal structure of iodic acid has been determined recently by Rogers and Helmholz[1] and they state that the crystalline acid is an aggregate of HIO_3 molecules held together by hydrogen bonds and that the iodate group is pyramidal.

The variation of physico-chemical properties of the aq. solution of the acid with concentration has been the subject of study for some time by Nayar and

1) Rogers and Helmholz: J. Am. Chem. Soc., **63**, (1941) 278.

co-workers[2]. Their results indicate definite breaks in the curves of the various physical properties at concentrations of 0.09 N and 0.04 N. According to them a concentrated solution of the acid contains mainly trimeric molecules $(HIO_3)_3$ which gradually change into dimers $(HIO_3)_2$ and then into monomers (HIO_3) as dilution increases. The breaks in the curves are attributed to transitions from one kind of molecule to another.

The theoretical structure of iodate ion has been discussed from the ionic and quantum mechanical point of view by Zachariasen[3] and from the shared-electronic point of view by Huggins[4].

The Raman spectrum of the acid and its salts has been investigated by a number of workers[5]-[13]. While there is general agreement between the results obtained, there is a great deal of discrepancy in the number of lines obtained and the frequencies measured by individual workers.

While there are fairly comprehensive data for concentrated solutions up to 18 N, the lowest concentration of the acid solution studied by the method of Raman spectra is 0.1 N. As pointed out before, the physico-chemical properties of the acid solution give transition points at 0.09 N and 0.04 N. Up to the present time, Raman spectra of iodic acid at these concentrations have not been studied. The present paper deals with an attempt to obtain the Raman spectra at different concentrations of the acid solution, including these particular regions.

2. Experimental

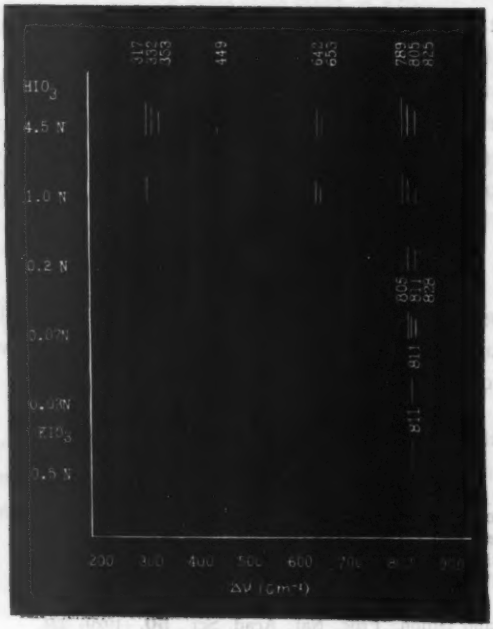
Iodic acid crystals, used were of the Kahlbaum analytical quality. They were further purified by recrystallisation, and the solutions were made in the freshly distilled conductivity water.

2) Nayar and Gairola: Z. Anorg. Chem., **220**, (1943) 163.
Nayar and Sharma: ibid., **220**, (1934) 169.
Nayar and others: ibid., **220**, (1939) 217.
Nayar and Mundle: Current Science., **10**, (1941) 76.
3) Zachariasen Physical: Review., **37**, (1931) 105.
Zachariasen: ibid., **37**, (1931) 775.
4) Huggins: ibid., **37**, (1931) 447.
Huggins: ibid., **37**, (1931) 1177.
5) Nisi: Jap. J, Phy., **5**, (1929) 119.
6) Dickinson and Dillon: Proc. Nat. Acad. Sci., **50**, (1929) 334.
7) Krishnamurti, P.: Ind. J, Phy., **5**, (1930) 633.
8) Woodward: Phy. Zeits., **32**, (1931) 680.
9) Nayar and Sharma, loc. cit.
10) Venkateswaran, C. S.: Proc. Ind. Acad. Sci., **2**, (1935) 119.
11) Shen, Yao and Wu: Phy. Rev., **51**, (1937) 235.
12) Fonteyne, R.: Natuurwetensch Tijds., **21**, (1939) 141.
13) Kujumzelis: Zeits, f. Phy. **110**, (1938) 760.

The experimental arrangement was the one usually adopted. The bulb of Wood's tube was placed very near the slit of the spectrograph. Light from a quartz mercury arc was focussed by a glass condenser on the unblackened straight portion of the Raman tube. The spectra were taken at the room tempeature using Fuess glass spectrograph.

Care was taken to run the arc at low current which helps to minimise the background. Ilford backed H.P. plates were used for photographing the spectra. The lines were measured by means of Hilger L 13 micrometer in comparison with an iron spectrum taken in the middle of the Raman spectrum and then the wavelengths were calculated by employing Hartmann's interpolation formula.

Microphotometric records of all the plates were obtained enabling one to study the structure of the various bands, to resolve them into their components and to obtain an idea of their relative intensities. Zeiss microphotometer was used.



Graphical Representation

3. Results

The following tables give Raman shifts and their relative intensities. The results of other main workers are also given. The exciting line is λ 4358.34A.

Iodic acid—4.5 N (aq)

Nayar and Sharma 5N	Shen. Yao and Ww 6 N	Venkateswaran 4.5 N	Author
—	—	—	317.2 (7)
—	330	328	331.6 (7)
358	390	377	354.0 (6)
—	—	—	449.3 (1)
659	—	644	642.3 (4)
—	—	—	653.4 (3)
—	779	789	789.0 (10)
—	—	796	806.2 (8)
822	826	823	826.0 (6)

Iodic acid—1 N (aq)

358	—	328	318.5 (4)
659	—	644	641.6 (3)
			653.8 (2)
		796	785.0 (10)
		799	806.8 (9)
822	—	819	823.9 (7)

Iodic acid—0.2 N (aq)

794		802	804.5 (5)
			823.8 (3)

Iodic acid and KIO_3 solutions.

Concentration	Raman Shift
0.07 N	804.4 (5), 811.8 (4), 828.3 (2)
0.03 N	811.3 (w)
KIO_3—0.2 N	811.4 (w)

4. Discussion of results

Concentrated solutions

A 4.5 N solution gives three Raman bands at about $\Delta\nu$ 330, 640 and 800, of which the last one is the broadest and most intense. These split up into various component frequencies shown.

A 1N solution gives essentially the same spectrum as the more concentrated one, with the important difference that the bands at 330 and 640 are less intense than before. At 0.2 N they are completely absent. This shows that these two bands consisting of five lines viz $\Delta\nu$ 317, 331, 354, 642, 653 should be attributed

to the vibrations of the highest polymer $(HIO_3)_3$.

Line $\Delta\nu$ 789

Of the three components of the band at $\Delta\nu$ 800, the frequency $\Delta\nu$ 789 being the lowest, represents a vibration of the I—O linkage in $(HIO_3)_3$—a three-coordinated structure of the iodic acid molecule. The fact, that this is the most prominent line in concentrated solutions and that with dilution it gradually becomes relatively weaker and that at 0.2 N and below, it disappears totally, is in keeping with the above conclusion.

Line $\Delta\nu$ 806

This frequency corresponds to the same oscillation in the two-coordinated structure of the iodic acid molecule $(HIO_3)_2$. It is to be noted that at 0.2 N and 0.07 N this is the most prominent line. Some of the previous workers have attributed this line to the IO_3^- ion. That this is not probable can be seen from the fact that the frequency $\Delta\nu$ 811 obtained with KIO_3 solution is not present in the concentrated solution of the acid.

From conductivity measurements Davies[14] has shown that even at a dilution of 0.001 N iodic acid is not completely ionised, which means that at the high concentrations used by the previous workers we should hardly expect free IO_3^- ions to be present, at any rate not in sufficient concentration to yield the characteristic Raman line.

The line $\Delta\nu$ 826

This line with the highest frequency shift, should on the same reasoning be attributed to the same I—O oscillation in the lowest polymer viz (HIO_3). But it should be remembered that such a molecule can exist only in cocentrated solution along with other polymerised molecules. Its existence in the free condition is rather doubtful, because from the curves of the physico-chemical properties HIO_3 molecules can presumably exist free from other polymers only below 0.04 N. But at this high dilution the acid must be ionised to a great extent. In other words the Raman frequency characteristic of the monomer should be expected to be shown only by the acid solution down to the concentration of 0.04 N. The line $\Delta\nu$ 826 is the only one which is present at all concentrations down to 0.07 N.

In his interpretation, Venkateswaran has attributed the line $\Delta\nu$ 823 to the $I_2O_9^{--}$ ion and the line $\Delta\nu$ 796 to the IO_3^- ion. It is rather difficult to imagine how there can be two different ions of the type $I_2O_9^{--}$ and IO_3^- existing side by side in the same solution and that too in a concentrated one. Depolymerisation and ionisation should take place step by step.

14) Davies: J. Phy. Chem., **29**, (1925) 973.

Dilute solutions

In the investigations of the physico-chemical properties of the acid solution, the course of depolymerisation of the trimeric molecules of the acid has been pictured as:—

$$\frac{1}{3}(HIO_3)_3 \xrightarrow[0.09\,N]{} \frac{1}{2}(HIO_3)_2 \xrightarrow[0.04\,N]{} (HIO_3) \downarrow H^+ + IO_3^-$$

If the interpretation of the transition points is correct, it is only below 0.04 N, that IO_3^- ions exist free from the influence of all polymers. This being so, a 0.03 N solution should be presumed to give Raman spectrum of iodate ions only.

0.2 N solution

In the 4.5 N solution the line $\Delta\nu$ 789 was the most intense and the one at $\Delta\nu$ 806 was of medium intensity, on the other hand at 0.2 N it is found that $\Delta\nu$ 789 is absent while the line $\Delta\nu$ 804 assigned to $(HIO_3)_2$ becomes the most intense.

This means that at this dilution trimeric molecules $(HIO_3)_3$ are absent while $(HIO_3)_2$ predominate. The presence of a faint companion at $\Delta\nu$ 824 shows that along with $(HIO_3)_2$ a small number of (HIO_3) molecules are also present.

0.07 N solution

Here again, the most prominent line is $\Delta\nu$ 804 showing that the majority of molecules are of the type $(HIO_3)_2$. The presence of the line $\Delta\nu$ 828 shows that (HIO_3) molecules are present at this dilution also.

But there is for the first time also a third line which has made its appearance as a faint companion to $\Delta\nu$ 804 viz $\Delta\nu$ 811.8. This shows that some free IO_3^- ions also make their appearance at this dilution.

0.03 N solution

At this dilution only one line at $\Delta\nu$ 811 is obtained and all the other lines present at higher concentrations have disappeared.

This can be explained by assuming that there is a complete change in the constitution of the acid as we pass down from 0.07 N to 0.03 N. At 0.03 N all the $(HIO_3)_2$ molecules are converted into (HIO_3) type, which again on account of the high dilution at 0.03 N, immediately break up into H^+ and IO_3^- ions. Hence the line $\Delta\nu$ 811.3 obtained at 0.03 N, should be considered as due to IO_3^- ions.

This is strongly supported by the fact that a KIO_3 solution gives exactly the same line at $\Delta\nu$ 811.4—a line which is definitely due to IO_3^- ions.

In his discussion on the structure of iodates, Venkateswaran[15] based his arguments on the Raman spectrum obtained with $LiIO_3$ solution. It is well known that Lithium, in contrast to other alkali ions, tends to form covalent bonds almost like hydrogen and hence the IO_3 group in $LiIO_3$ should be expected to be slightly distorted by the Li atom (according to Fajan's theory) and will thus behave differently from the IO_3 ions obtaining in KIO_3 solution. In fact, $LiIO_3$ will behave more like HIO_3 than like KIO_3. In other words a study of $LiIO_3$ solution cannot give us accurate information about the structure of the IO_3^- ion.

This is further supported by the crystal structure data of $LiIO_3$ according to which simple or complex iodate ions do not exist in $LiIO_3$ crystals.

In conclusion the author wishes to express his gratitude and sincere thanks to Dr. P. N. Sharma and to late Mr. M. R. Nayar for their kind directions during the progress of the work.

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15) Venkateswaran, C. S.: Proc. Ind. Acad. Sci., **7A**, (1938) 152.

Note: After the present paper was written up and a short note of the same sent for publication (Saraf; Current Science, **11**, (1942) 101.), a paper on the same subject by N. R. Rao (Rao; Ind. J. Phys, **16**, (1942) 71) appeared. The lowest concentration used by Rao was 0.4 N and according to him the band at $\Delta\nu$ 800 obtained with 6 N solution, consists of only one component and that IO_3^- ions exist at 1.6 N and below.

On the other hand the line given by KIO_3 solution viz 810 (Rao) agrees with the author's value. Besides the views held by Rao that $I_2O_6^{--}$ ions do not exist and that $\Delta\nu$ 825 should be attributed to HIO_3 molecule, are in agreement with the author's conclusions.

Exchange